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SENSITIVITY OF NON-SUPPRESSED ION CHROMATOGRAPHY USING DIVALENT ORGANIC ACIDS AS ELUENTS

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SUMMARY

Aqueous organic acids such as tartaric and malic acids were effective as eluents for some rapidly eluted anions in non-suppressed ion chromatography. For these eluents, the equation for the sensitivity was derived and the response of the conductivity detector was calculated. Reasonable agreement was found between the observed and calculated sensitivities.

INTRODUCTION

In the analysis of anions by suppressed ion chromatography, a low capacity ion-exchange resin column and a suppressor system are used in order to separate the ions and to lower the conductivity of the eluent, *e.g.*, a carbonate[1–3] or borate[4] solution. This method has been widely used in various fields of scientific research. On the other hand, Gjerde and co-workers[5–8] reported that anions can be separated and detected by using a conductivity detector connected directly to the separation column with an eluent of low conductance, such as a phthalate or benzoate solution. However, the sensitivity of this single column system is generally lower than that with a suppressed system. In this regard, Gjerde and Fritz[7] pointed out that the sensitivity of the conductometric detector depended on the magnitude of the ionic equivalent conductance of a counter cation in the eluent (H^+ is the most preferable). It also depends on the difference between the equivalent conductances of the eluent anion and the solute anion when both anions are completely dissociated. An eluent which seems approximately to satisfy this condition is phthalate solution, which has been found to be one of the most successful eluents in single column ion chromatography.

Likewise, we found that aqueous organic acid solutions, such as tartaric acid and malic acid, are effective eluents for some rapidly eluted anions. In this paper, the range of application and sensitivity of these eluents is discussed, and the calculated sensitivity is compared with the experimental results.

EXPERIMENTAL

Apparatus

A Toyo Soda non-suppressed ion chromatograph HLC-601 equipped with an anion-exchange column packed with TSKgel IC-Anion-PW (particle size $10 \pm 2 \mu m$, capacity 0.03 ± 0.005 mequiv./g, 50×4.6 mm I.D.) was used. The experimental conditions are shown in Table I. A Deleca impedance bridge Model 12K was used for measurement of the ionic equivalent conductance of sodium tartrate.

TABLE I

EXPERIMENTAL CONDITIONS

Instrument	HLC-601 (Toyo Soda Manufacturing Co.)
Separation column	TSK GEL IC-Anion-PW (50×4.6 mm I.D.)
Oven temperature	25°C
Flow-rate	1.2 ml/min
Pressure	15–20 kg/cm²
Sample loop	100 μl

Reagents

Standard solutions were prepared by dissolving the potassium salt of each anion, dried *in vacuo* at 110°C overnight, in pure water. Distilled deionized water was used.

The eluents were prepared by dissolving guaranteed reagent L-tartaric acid or D,L-malic acid in pure water, and adjusting the pH with 0.1 M potassium hydroxide solution.

RESULTS AND DISCUSSION

Elution of anions with a dibasic organic acid

Tartaric acid and malic acid were chosen as dibasic organic acid eluents having specific elution characteristics for anions which are rapidly eluted from conventional ion-exchange resins. Figs. 1 and 2 show the ion chromatograms of 10 ppm of phosphate, fluoride, chloride and bromate ions eluted with tartaric and malic acid, respectively. The peak of the fluoride ion was not identified in the dip peaks. It was confirmed that phosphate ion was dissolved in the form of $H_2PO_4^-$ at the pH of both eluents. The detection limits (the concentration corresponding to twice the value of the baseline noise) of F^-, $H_2PO_4^-$, BrO_3^- and Cl^- with 3 mM malic acid eluent were 10, 10 (as PO_4^{3-}), 21 and 3.4 ppb, respectively. On the other hand, it was necessary for the pH of the eluent to be adjusted over 4 for the analysis of nitrate, bromide and sulphate ions, which were more slowly eluted than chloride ion. However, in this case, lowering of sensitivity was unavoidable because of the presence of the counter cation (K^+) in addition to H^+, as already mentioned.

Effect of eluent concentration

The effect of the concentration of tartaric acid on the elution and sensitivity of each anion was investigated. Fig. 3 shows the relationship between the concentra-
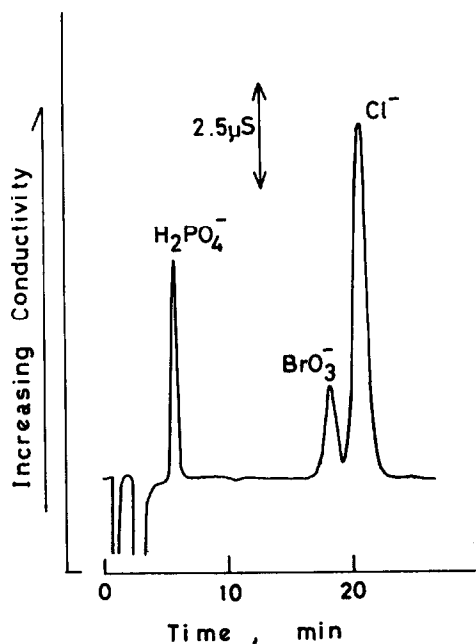
Fig. 1. Separation of Cl⁻, BrO₃⁻ and H₂PO₄⁻. Eluent: 2 mM tartaric acid. Resin: TSKgel IC-Anion-PW. Flow-rate: 1.2 ml/min. Sample: 10 ppm of each anion.
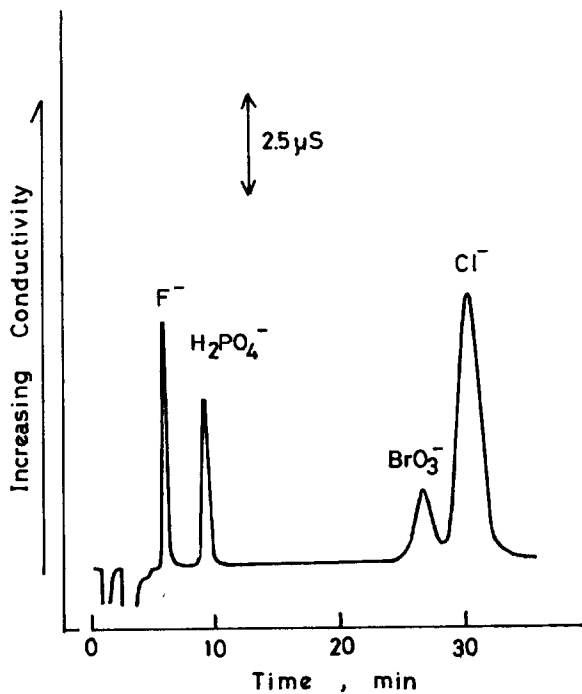

Fig. 2. Separation of Cl⁻, BrO₃⁻, H₂PO₄⁻ and F⁻. Eluent: 3 mM malic acid. Other conditions as in Fig 1.
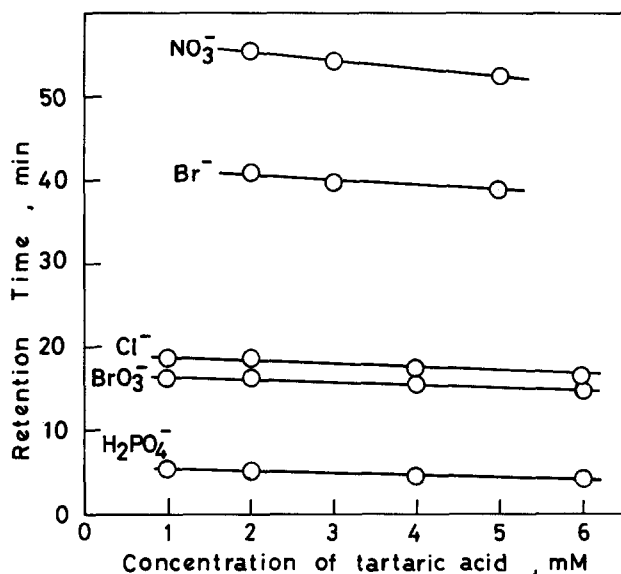
Fig. 3. Variation of retention times with the eluent (2 mM tartaric acid) concentration. Conditions as in Fig. 1.

tion of tartaric acid and the retention times of the anions. Although the retention time decreases slightly with increasing concentration of tartaric acid, large change were not observed. This behaviour is explained by the fact that the concentration of tartrate ion (tart^{2-}), which contributes to the elution, changes little upon depression of the dissociation of the eluent with increasing concentration.
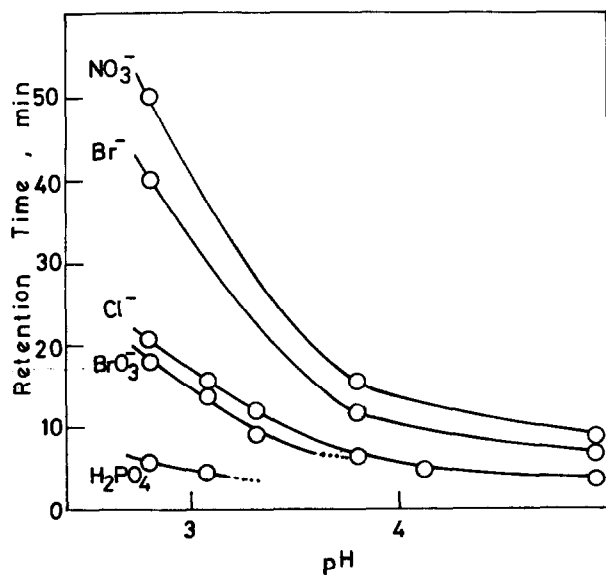

Fig. 4. Variation of retention times with the eluent (2 mM tartaric acid) pH. Conditions as in Fig. 1.
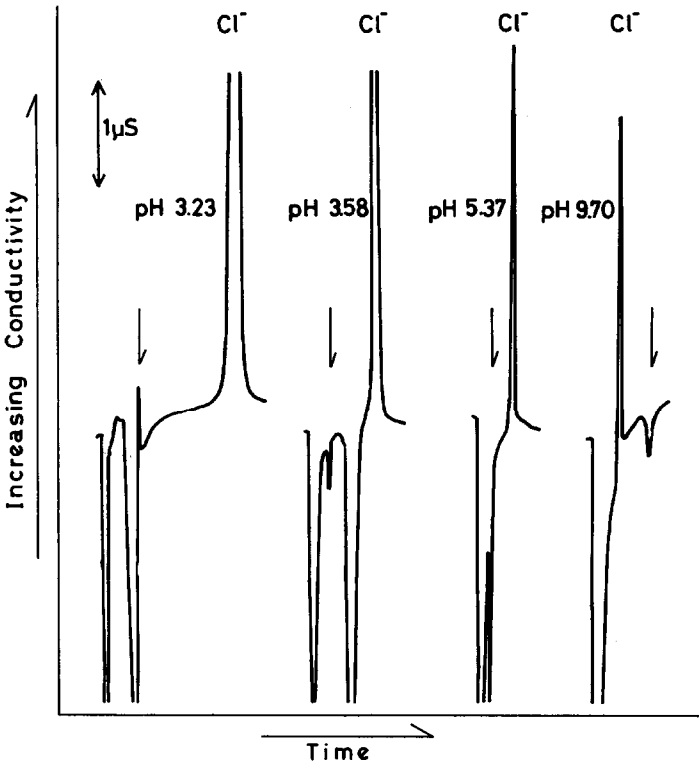
Fig. 5. Ion chromatograms of phosphate and chloride ions. The arrows show the phosphate peaks. Conditions as in Fig. 1.
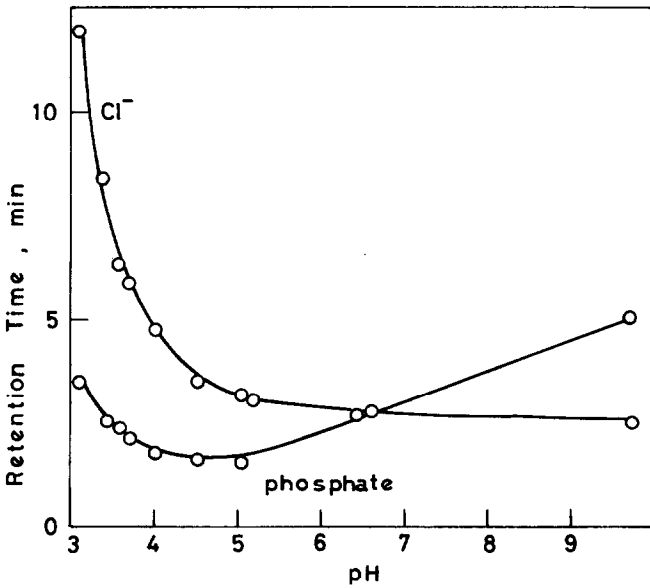

Fig. 6. Variation of retention times of phosphate and chloride ions with the eluent pH. Conditions as in Fig. 1.

Effect of eluent pH

The elution behaviour of each anion was investigated at various pH values of 2 mM tartaric acid eluent. Fig. 4 shows the relationship between the retention time of each anion and the eluent pH. The retention times marked decreased with increasing pH accompanying the increase in concentration of $tart^{2-}$. The chloride and bromate ions were not completely separated at pH > 4, and a positive peak for phosphate ion was not observed at pH > 3.3. Fig. 5 shows the chromatograms of 10 ppm of chloride ion and phosphate ion at various eluent pH values. The peak of phosphate ion disappeared at pH 3.23, and a negative peak appeared at pH 3.70 growing in intensity with increasing pH. Finally, the retention time of the phosphate ion was increased, and the order of elution of the phosphate and chloride ions was reversed at pH 9.70 (the phosphate ion was eluted faster than the chloride ion at low pH). Fig. 6 shows the relationship between the retention times of chloride and phosphate ions and pH over a wider pH range than that in Fig. 4. The retention time of chloride ion decreased with increasing concentration of $tart^{2-}$ and became constant when the degree of dissociation of $tart^{2-}$ was 1. On the other hand, the retention time of phosphate ion became large at pH > 4.5. This shows that the second dissociation to HPO_4^{2-} started at this pH.

Sensitivity of conductivity detector with a divalent organic acid as eluent

Gjerde *et al.* investigated theoretically the sensitivity of the conductivity detector for monovalent eluents. On the basis of those results, we examined the sensitivity of the divalent organic acid eluents.

The specific conductance of a solution, Λ, is represented by

$$\Lambda = (\lambda^+ + \lambda^-)\alpha C/1000k \tag{1}$$

where α is the degree of dissociation of the solute, C is the concentration of the solute, k is the cell constant and λ^+ and λ^- are the limiting equivalent conductances of the cation and anion, respectively. The background conductance, Λ', when there is no sample solute, and the solute band conductance, Λ'', are given by eqns. 2 and 3, respectively

$$\Lambda' = (\lambda_e^+ + \lambda_{HA}^-)\alpha_1 C_e + (2\lambda_e^+ + \lambda_A^-)\alpha_2 C_e/1000k \tag{2}$$

$$\Lambda'' = [(\lambda_s^+ + \lambda_s^-)\alpha_s C_s + (\lambda_e^+ + \lambda_{HA}^-)(C_e - C_s'\alpha_s)\alpha_1 +$$
$$+ (2\lambda_e^+ + \lambda_A^-)(C_e - C_s''\alpha_s/2)\alpha_2]/1000k \tag{3}$$

where e and s represent the eluent and solute, HA and A are the eluent anions, α_1 and α_2 are $[HA^-]/C_e$ and $[A^{2-}]/C_e$ and C_s' and C_s'' are the solute concentrations eluted with HA^- and A^{2-}, respectively.

First, the sample is concentrated at the front part of the separation column and is then eluted with an eluent. Therefore, $\lambda_s^+ = \lambda_e^+ = \lambda^+$. The difference between eqns. 2 and 3 gives the response of the conductivity detector to the elution of a sample

$$\Delta\Lambda = \Lambda'' - \Lambda' = [(\lambda_s^+ + \lambda_s^-) - (\lambda^+ + \lambda_{HA}^-)m\alpha_1/(1 + m) -$$
$$(2\lambda^+ + \lambda_A^-)\alpha_2/2(1 + m)]C_s\alpha_s/1000k \tag{4}$$

where $m = C'_s/C''_s$. If $\alpha_1 = \alpha_2 = 0$ and $m = 0$, $\Delta\Lambda$ is given by:

$$\Delta\Lambda = (\lambda_s^- - \lambda_e^-/2)\alpha_s C_s/1000k \qquad (5)$$

If $\alpha_2 = 0$ and $m \rightarrow \infty$, $\Delta\Lambda$ is given by:

$$\Delta\Lambda = [(1 - \alpha_1)\lambda^+ + \lambda_s^- - \lambda_{\overline{HA}}\alpha_1]\alpha_s C_s/1000k \qquad (6)$$

When the difference between pK_1 (= 3.04) and pK_2 (= 4.37) is small, as in tartaric acid, eqn. 6 is invalid. Therefore, the sensitivity must be calculated by eqn. 4 using tartaric acid as eluent.

Comparison of observed and calculated sensitivity

The calculated sensitivity was compared with the experimental results using tartaric acid as eluent. In this case, the following values were used: $\lambda_{\overline{HA}} = 32.2$ Ω^{-1} cm^2 mol^{-1} (ref. 9); λ_A^-, determined from Kohlrausch's equation by using the measured conductance, $= 118$ Ω^{-1} cm^2 mol^{-1}. The ratio, m, of the solute concentrations eluted with HA$^-$ and A^{2-} was determined by the following procedure. If it is assumed that the elution strength of one molecule of A^{2-} corresponds to that of x molecules of HA$^-$, the value of x can be calculated by normalizing to unity the slope
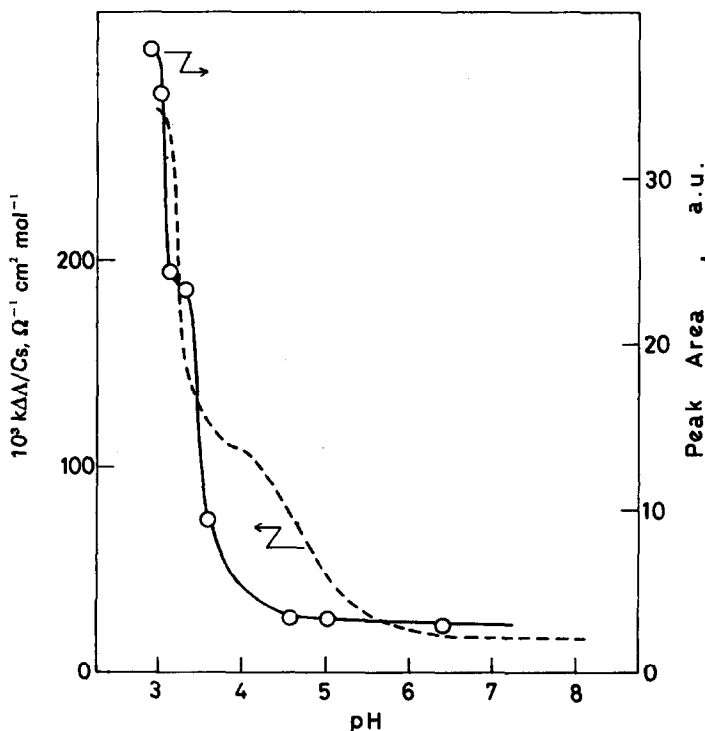

Fig. 7. Relationship between the peak area of chloride and the eluent pH. The broken line represents $1000k\Delta\Lambda/C_s$. Conditions as in Fig. 1.
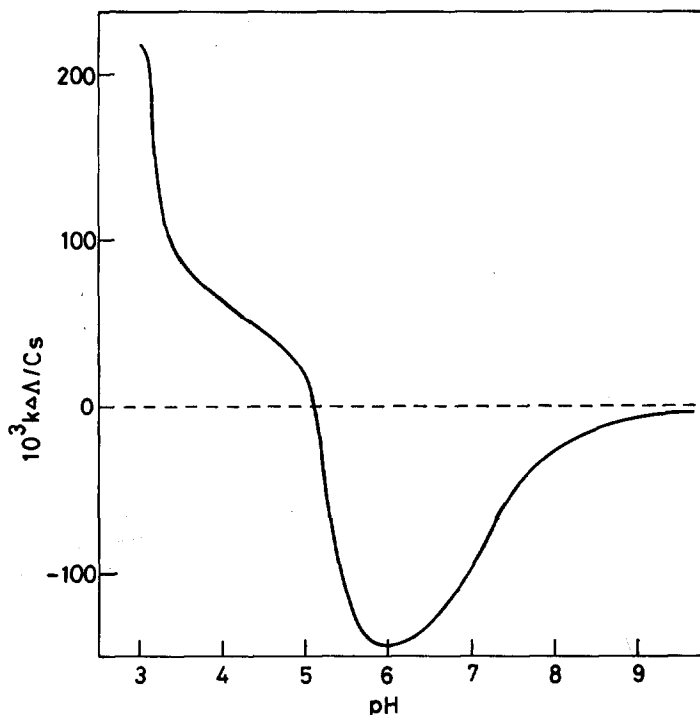
Fig. 8. Variation of $1000k\Delta A/C_s$ of phosphate with the eluent pH. Conditions as in Fig. 1.

of the log[HA] *vs.* log($t_R - t_0$) plot for chloride ion. Here t_R and t_0 are the retention times of the solute ion and the unabsorbed molecule on the ion-exchange resin, respectively. Consequently, x was found to be 4.5. ΔA values for chloride ions were calculated and plotted against the eluent pH, Fig. 7. The solid line and the broken line are respectively the peak area and $1000k\Delta A/C_s$ for chloride ion. Fig. 8 shows the calculated value of variation of $1000k\Delta A/C_s$ for phosphate ion. Although the calculated values for chloride are shifted to higher pH values, there is reasonable agreement between the observed and calculated values. It seems that the difference between the calculated and observed values is caused by using concentrations instead of activities.

In conclusion, the sensitivity can be predicted in non-suppressed ion chromatography. It is considered that higher sensitivities are obtained by the use of an eluent having a high elution strength, in which no counter cations other than H^+ exist.

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