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## Note

### Modeling of analyte response to changing eluent composition in suppressed ion chromatography

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Suppressed ion chromatography, first presented in 1975<sup>1</sup>, has rapidly developed into a widely accepted means of quantitating aqueous phase anion content. As is the case with all chromatographic techniques, the most effective utilization of ion chromatography requires the ability to predict the behavior of analytes as a function of changing operational parameters and to optimize interspecies resolution in minimal total analysis time. Attempts to model the ion chromatographic process can be divided into those which consider the eluent to consist of a single active species<sup>2</sup> and models that consider the eluent to consist of a group of interacting species<sup>3</sup>.

For suppressed chromatography the eluents are carbonate, bicarbonate and hydroxide ions, all of which participate in the exchange process. Thus the single eluent model is inapplicable. This report models the elution behavior of  $\text{Cl}^-$ ,  $\text{NO}_3^-$  and  $\text{SO}_4^{2-}$  using the Hoover model<sup>3</sup>, modified to include solution and resin activities. Mathematical manipulations permit the elimination of resin activities from the pertinent equations, and solution activities coefficients were predicted using the extended Debye-Huckel equation. Changing eluent compositions are utilized and optimum analytical conditions are determined from window diagrams.

#### EXPERIMENTAL

All chromatograms were obtained with a Dionex Model 14 ion chromatograph equipped with standard  $500 \times 3$  mm I.D. anion separator and  $250 \times 6$  mm I.D. suppressor columns. Chromatograms were recorded on a Honeywell flatbed dual-pen strip chart recorder. Sample loop volume was 0.10 ml, detector response was maintained at 10 m $\Omega$ /cm full scale deflection and laboratory temperature was maintained at  $22 \pm 1^\circ\text{C}$ .

Eluents used throughout this study were prepared by dissolution of the appropriate amount of  $\text{Na}_2\text{CO}_3$  and  $\text{NaHCO}_3$  in deionized water. Eluents were allowed to stabilize for a period of 12-24 h before use. The pH of these eluents was measured just prior to their use. All samples were prepared by dilution of single analyte stock solutions with the  $\text{Na}_2\text{CO}_3$  and  $\text{NaHCO}_3$  solutions. Stock solutions for chloride and nitrate were prepared by dissolution of their sodium salts in deionized water, and the sulfate standard was a 0.010 M sulfuric acid solution prepared by the Hach Chemical Company: the normality of this solution was confirmed by titration with a standard

base. All salts used were reagent grade and all analyses were performed in triplicate. Reduced retention times are the measured times minus the void volume equivalent.

## RESULTS AND DISCUSSION

Modifying the Hoover treatment of ion chromatographic separation for solution activities produces a relationship between retention volume ( $U$ ) and eluent composition as shown below.

For a monovalent analyte.

$$U_1 = \left( \frac{K_{11}}{X_{21}} \right) \frac{E_1 + X_{31}E_3}{4E_2} \left( \sqrt{1 + \frac{8X_{21}QE_2}{(E_1 + X_{31}E_3)^2}} - 1 \right) \quad (1)$$

and for a divalent analyte,

$$U_2 = \frac{K_{21}}{(X_{21})^2} \frac{(E_1 + X_{31}E_3)^2}{8E_2^2} \left( 1 + \frac{8X_{21}QE_2}{2(E_1 + X_{31}E_3)^2} - \sqrt{1 + \frac{8X_{21}QE_2}{(E_1 + X_{31}E_3)^2}} \right) \quad (2)$$

where the  $K$  values are selectivity coefficients relating the analyte and eluent species and  $X$  values are selectivity coefficients relating the eluent species to one another.  $Q$  is the column capacity,  $E$  represents solution phase activities of eluent species and the subscripts 1, 2 and 3 refer to the species  $\text{HCO}_3^-$ ,  $\text{CO}_3^{2-}$  and  $\text{OH}^-$  respectively.

The effect of eluent composition on the relative retention of  $\text{Cl}^-$ ,  $\text{NO}_3^-$  and  $\text{SO}_4^{2-}$ , is shown in Table I. Observed trends include: (1) sulfate is most affected by

TABLE I  
ELUENT COMPOSITION AND ANALYTE RETENTION TIMES

Eluent	Total carbonate ( $10^{-3}$ M)	pH	Ionic strength ( $10^{-3}$ M)	Activity distribution ( $10^{-3}$ M)			Retention time (min)		
				$\text{OH}^-$	$\text{HCO}_3^-$	$\text{CO}_3^{2-}$	$\text{Cl}^-$	$\text{NO}_3^-$	$\text{SO}_4^{2-}$
1	2.0	10.10	5.0	0.13	1.05	0.66	5.2	20.8	25.6
2	4.0	9.85	6.0	0.07	2.50	0.94	4.8	19.2	13.5
3	5.0	10.10	9.9	0.13	2.59	1.55	4.0	14.8	12.6
4	8.0	11.40	17.1	0.24	2.59	3.12	3.3	11.2	11.5
5	11.0	10.20	19.8	0.17	4.32	3.80	3.2	10.6	9.6
6	14.0	10.05	25.0	0.11	6.56	3.52	3.1	9.9	10.6
7	10.0	10.55	23.1	0.36	2.25	4.15	3.2	9.6	8.8
8	17.0	9.90	25.8	0.08	9.02	3.51	3.1	9.5	7.6
9	16.0	10.15	29.2	0.15	6.22	4.65	3.0	9.0	6.6
10	12.0	10.15	31.5	0.55	1.89	5.26	2.9	8.7	4.0
11	21.0	10.15	39.6	0.15	7.93	5.82	2.1	7.6	—
12	42.0	10.25	79.2	0.18	13.15	10.78	2.3	6.2	—

TABLE II  
SELECTIVITY COEFFICIENTS

	$Cl^-$	$NO_3^-$	$SO_4^{2-}$
$X_{21}$	5.0	5.0	5.0
$X_{31}$	0.01	0.01	0.01
$K_{i1}$	3.02	16.8	18.5

the eluent composition changes; (2) changes in carbonate concentration have a larger effect on analyte retention than do concentration changes in the other eluent species; (3) in cases where eluent ionic strength is similar, pH had no effect on elution characteristics. The first two observations have been explained in terms of ionic site/charge effects<sup>4</sup>, while the third point suggests a small affinity between the resin sites and the hydroxide eluent.

Utilization of eqns. 1 and 2 requires a determination of the selectivity coefficients. Substitution of known eluent compositions and retention times for each analyte into these expressions produces a set of simultaneous equations containing these coefficients as dependent variables. The system of equations is solved by simplex optimization, first described by Long<sup>5</sup> and used by Hoover<sup>3</sup>. The algorithm is described by O'Neill<sup>6</sup>. Values for the calculated selectivity coefficients are listed in Table

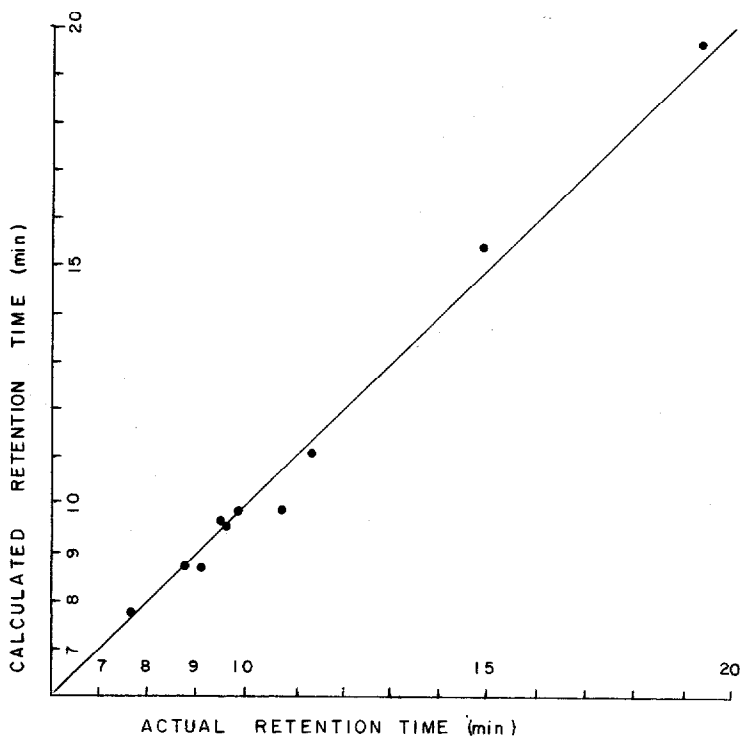


Fig. 1. Comparison of observed and calculated retention times for  $NO_3^-$ . Slope = 1.128; intercept = -1.35;  $r = 0.996$ ; av. R.S.D. = 0.00; av. |R.S.D.| = 2.75.

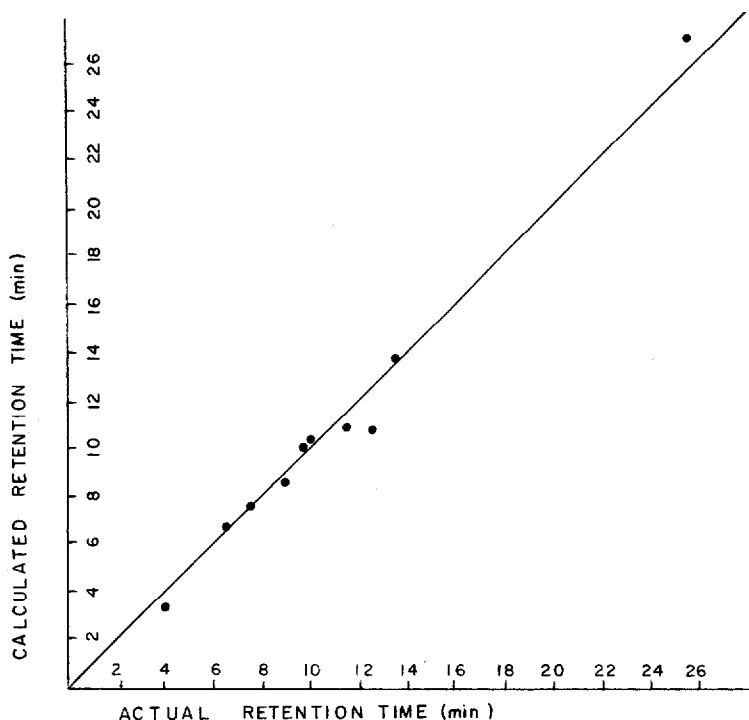


Fig. 2. Comparison of observed and calculated retention times for  $\text{SO}_4^{2-}$ . Slope = 1.059; intercept =  $-0.68$ ;  $r = 0.994$ ; av. R.S.D. =  $-0.07$ ; av. |R.S.D.| = 4.01.

II. The magnitude of the  $X_{31}$  coefficient reflects the columns limited affinity for hydroxide, while the magnitude of  $X_{21}$  is consistent with the observation that carbonate affects elution properties more strongly than does bicarbonate. The trend in the magnitude of the  $K_{i1}$  values reflects the elution order of the analytes with shorter retention times providing lower selectivity coefficients.

The ability of the model accurately to characterize the chromatographic process is illustrated in Figs. 1 and 2, the plots of calculated *versus* observed retention times. In these figures, the line represents a one-to-one correlation between observed and predicted behavior. The small magnitude of the average point-by-point relative standard deviation between observed and calculated retention times indicates lack of skew in the data. The absolute magnitude of the average deviation (av. |R.S.D. |) is equivalent to the experimental error. In the chloride case there is a definite skew to the data which is believed to be due to an interaction between the anion and the suppressor column. In addition to modeling analyte behavior, it is of practical interest to be able to optimize the chromatographic behavior by maximizing interspecies resolution and minimizing total analysis time. Window diagrams, where relative retention characteristics of a pair of analytes are plotted as a function of an operational variable, have been successfully applied to the optimization of other chromatographic systems<sup>7-10</sup>. The relative behavior of an analyte pair is described in terms of the reduced retention ratio  $\alpha$  which is defined as

$$\alpha = \frac{t_{RA} - t_{RO}}{t_{RB} - t_{RO}} \quad (3)$$

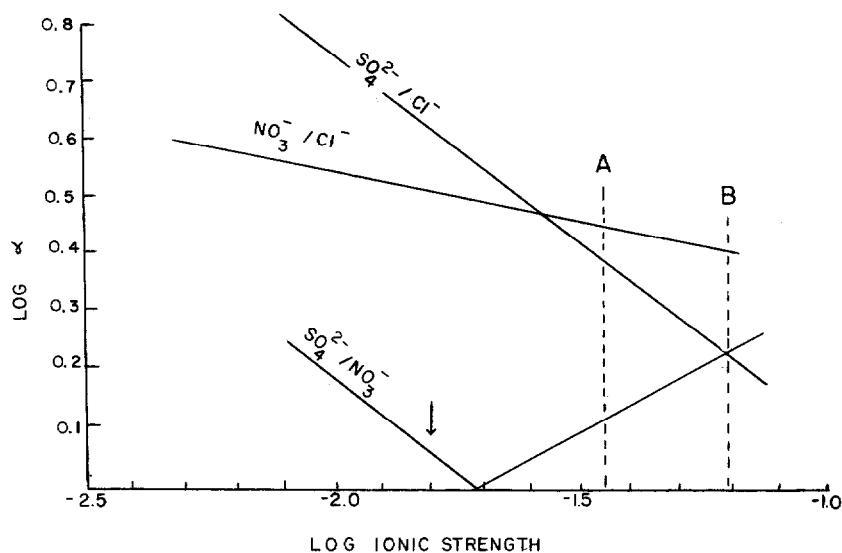


Fig. 3. Window diagram for the suppressed system. The arrow denotes the composition of the test eluent.

where  $t_{RA}$  and  $t_{RB}$  are the measured retention times for analyte A and B and  $t_{RO}$  is the void volume equivalent. Eluent composition is the system's variable and is expressed in terms of ionic strength ( $I$ ).

$$I = \frac{1}{2} \sum_i C_i Z^2 \quad (4)$$

$Z$  is the ionic charge and  $C_i$  is the concentration. Owing to the large range of eluent ionic strength, the window diagram is presented in logarithmic form (Fig. 3). The resulting diagram is interpreted as follows. At  $\alpha = 1$  ( $\log \alpha = 0$ ) the reduced retention times of the analytes are equivalent and peaks overlap; this occurs for the  $\text{SO}_4^{2-}/\text{NO}_3^-$  pair at  $\log I = -1.71$ ). As  $\log \alpha$  increases, the separation improves. Movement in a vertical direction as designated by the dashed line A in Fig. 3 provides intersection with the three lines. The first intersected line designates the pair of poorest resolution

TABLE III

CALCULATION OF TEST CASE RETENTION CHARACTERISTICS

Eluent consists of  $4.0 \cdot 10^{-3} M \text{NaHCO}_3$ ,  $4 \cdot 10^{-3} M \text{Na}_2\text{CO}_3$ , pH 10.25.

Species	Retention time (min)		
	Observed	Calculated	
		Window diagram	Equations
$\text{Cl}^-$	4.3	4.2	4.0
$\text{NO}_3^-$	13.3	13.3	13.4
$\text{SO}_4^{2-}$	14.9	15.0	14.7

and the last intersected line designates the pair of best separation. The composition designated by vertical line B provides the optimal separation for this system.

Table III documents the utilization of both window diagrams and eqns. 1 and 2 to predict the retention characteristics of  $\text{Cl}^-$ ,  $\text{NO}_3^-$  and  $\text{SO}_4^-$  in an eluent which was not used to generate selectivity coefficients. In all cases, the agreement between calculated and observed times is within experimental precision.

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