# Effect of temperature on retention and selectivity in ion chromatography of anions

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## Abstract

The temperature dependence of retention of a wide range of inorganic anions is studied on two commercially available ion exchangers (Dionex AS11 and AS14 columns). Anion retention exhibited both exothermic and endothermic behavior, such that varying the temperature from ambient to 60°C produced selectivity changes. The anions displayed three groupings of temperature dependence: weakly retained singly charged anions (e.g., iodate, bromate, nitrite, bromide and nitrate); multiply charged anions (sulfate, oxalate, phosphate and thiosulfate); and strongly retained singly charged anions (iodide, thiocyanate and perchlorate). Temperature was ineffective at changing the selectivity of retention between anions of the same grouping. However, significant selectivity changes, including elution order reversal, could be achieved between anions from different groupings.  © 2001 Elsevier Science B.V. All rights reserved.

*Keywords:* Temperature effects; Selectivity; Retention behavior; Inorganic anions

## 1. Introduction

Selectivity is of critical importance in developing a chromatographic method [1]. Significant changes in selectivity are obtained with modifications in the stationary phase type and mobile phase [2,3]. Therefore, ion-exchange selectivity is usually adjusted by changing the stationary phase [4]. Unfortunately, this approach is expensive. Although modification of the eluent is a cheaper and much simpler method, it has its disadvantages. Firstly, a change in the concentration or type of eluent will not alter the selectivity between analytes having the same charge as the eluent ion [5]. Secondly, optimization becomes increasingly difficult as the number of components in the eluent increases (e.g., carbonate–hydrogen car-

bonate eluents) [6]. Finally, in suppressed ion chromatography the choice of eluents is limited to those that can be suppressed (i.e., hydroxide, carbonate).

In recent years temperature has become an increasingly popular parameter in high-performance liquid chromatography (HPLC) method development, particularly for reversed-phase liquid chromatography (RPLC) [3]. The attractive features of using temperature for optimizing a chromatographic method are: it is experimentally easy to implement; it is applicable to both neutral and charged analytes; and it is easy to model. Despite the growing use of temperature in RPLC, temperature has been a relatively unexploited variable in ion-exchange chromatography. However, Rey and Pohl did demonstrate that column temperature was an effective means of increasing the separation between monovalent and divalent cations on a Dionex CS12A stationary phase [7]. Similarly, Pirogov et al. were able to alter the selectivity in a separation of halides by increasing

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the temperature from 25 to 60°C [8]. Further, a number of workers have noted changes in elution order upon altering the temperature of a separation [9,10].

This work explores the effect of temperature on the retention factors of inorganic anions on two commercially available ion chromatography columns (Dionex AS11 and AS14). The merits of using temperature to alter the selectivity of a separation are then discussed.

## 2. Experimental

### 2.1. Apparatus

A Beckman System Gold Model 125 dual piston pump (Beckman, Fullerton, CA, USA) was used to pump eluent at a flow-rate of 0.3 ml/min. Injections were performed manually with a Rheodyne 9125 (Rheodyne, Cotati, CA, USA) six-port injection valve fit with a 2-$\mu$l loop. All separations were performed on a Dionex AS11 strong base anion exchanger (250×2 mm I.D.) or a Dionex AS14 strong base anion exchanger (250×2 mm I.D.) (Dionex, Sunnyvale, CA, USA). Connecting tubing was 0.005 in. I.D. (in.=2.54 cm) polyether ether ketone (PEEK) (Upchurch Scientific, Oak Harbor, WA, USA).

All experiments were performed using suppressed conductivity detection with a Dionex AMMS-II suppressor and a CDM-3 conductivity detector. A constant pressure pump ($\cong 15$ p.s.i.; 1 p.s.i.= 6894.76 Pa) was used to pump 50 m$M$ sulfuric acid at a flow-rate of 5 ml/min through the suppressor. Data were collected using a Dionex AI-450 data acquisition system interfaced to a 486 microcomputer.

The column temperature was controlled to within 0.1°C using an Eppendorf CH-30 (Alltech, Deerfield, IL, USA) column heater equipped with a mobile phase preheater and controlled by an Eppendorf TC-50. Connections to/from the column heater tripled the amount of connecting tubing compared to what would have normally been used. However, the efficiencies achieved with the oven in place were comparable to those observed at room temperature

(23°C) without the column oven or extra connecting tubing.

### 2.2. Reagents

All reagent solutions were prepared using distilled deionized water (Nanopure Water System; Barnstead, Chicago, IL, USA). All chemicals were reagent-grade or better. Stock solutions of inorganic anions were prepared ($\cong 10^{-2}$ $M$) and diluted to the desired concentration ($\cong 10^{-5}$ $M$) before use. Bromate (Fisher, Nepean, Canada), nitrite (BDH, Toronto, Canada), thiosulfate (Anachemia, Toronto, Canada), perchlorate (Anachemia), iodide (BDH), sulfate (BDH) and phosphate (Fisher) were used as their sodium salts. Iodate (ACP, Montreal, Canada), bromide (Fisher), nitrate (BDH), oxalate (Matheson, Coleman & Bell, Norwood, OH, USA) and thiocyanate (Fisher) were used as their potassium salts. Sodium carbonate, sodium hydrogen carbonate and sodium hydroxide were obtained from BDH.

### 2.3. Procedure

Two eluents were used for all of the separations in this study: hydrogen carbonate–carbonate and hydroxide. Carbonate eluents were filtered through a 0.45-$\mu$m filter before use and were degassed by continually sparging with helium. Hydroxide eluents were prepared by adding the appropriate amount of a 50% (w/w) sodium hydroxide solution to 1 l of degassed, filtered (0.45 $\mu$m filter) 18 M$\Omega$ water (Barnstead Nanopure). Carbonate contamination was minimized by continually sparging with helium.

Temperature studies were conducted from 27 to 60°C. Temperatures higher than 60°C were not examined so as to avoid potential damage to the columns. The maximum temperature was chosen based on the work of others who also used Dionex columns [7,11]. According to Poppe and Kraak [12], the existence of temperature gradients in a column adversely affects the efficiency of a separation. Therefore, the column was allowed to equilibrate for approximately 30 min at the desired temperature. Also, narrow diameter columns were used to reduce the equilibration time of the system and minimize any temperature gradients in the column. The col-

umn void time was measured at each temperature using the water dip.

## 2.4. Calculations

Data analysis was performed using Microsoft Excel 97 software. The Regression function in the Data Analysis Tool Pak was used to obtain regression coefficients for the effect of temperature on retention.

# 3. Results and discussion

## 3.1. Van't Hoff plots

The effect of temperature on chromatographic retention is described by the general thermodynamic relationship governing equilibria:

$$\frac{d\ln k}{dT} = \frac{\Delta H^0}{RT^2} \tag{1}$$

where $k$ is the retention factor, $T$ is the temperature in Kelvin, $R$ is the universal gas constant and $\Delta H^0$ is the enthalpy of exchange. If $\Delta H^0$ is independent of temperature (which is usually true over a small temperature range), and the separation is performed under isocratic conditions, Eq. (1) can be integrated to:

$$\ln k = A - B/T \tag{2}$$

where $A$ and $B$ are constants for a particular analyte. According to Eq. (2), a plot of ln $k$ against the reciprocal of temperature (i.e., a van't Hoff plot) will be linear. As Eq. (2) has a similar form to the linear solvent strength model, computer-modeling programs such as Drylab can readily be used to model the effect of temperature [3]. This simplicity of modeling coupled with the instrumental ease of controlling column temperature has led to the increased use of temperature in optimizing RPLC separations [3,13–16].

Previous studies have observed that retention in ion-exchange chromatography obeys the simple thermodynamic relationships given in Eqs. (1) and (2) [11,17,18]. For instance, van't Hoff plots were linear over 25 to 56°C for metal ions retained on a
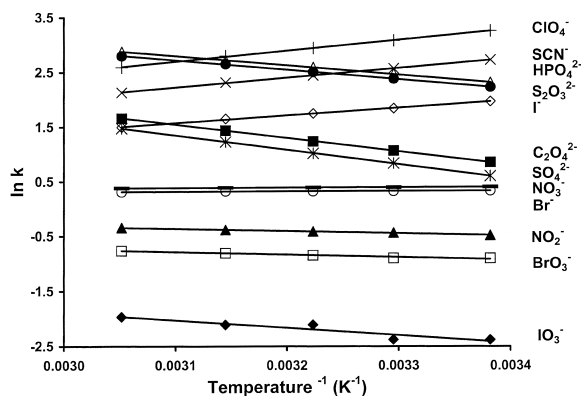


Fig. 1. Van't Hoff plots for anions separated on a Dionex AS11 column. A 12 m$M$ hydroxide eluent at 0.3 ml/min was used for the separation. The temperature range investigated was 27 to 60°C.

Wescan cation-exchange column [17]. Similarly, Smith et al. observed linear van't Hoff plots for common anions on a Dionex AS-4A column over the range 10 to 75°C [11]. However, over more extended temperature ranges (0–150°C) some nonlinearity in van't Hoff plots has been observed [10]. This minor nonlinearity in temperature dependence is similar to that observed by Mao and Carr in their RPLC studies over a temperature range of 30 to 130°C [19].

Figs. 1 and 2 show typical van't Hoff plots for anions separated on the Dionex AS11 and AS14
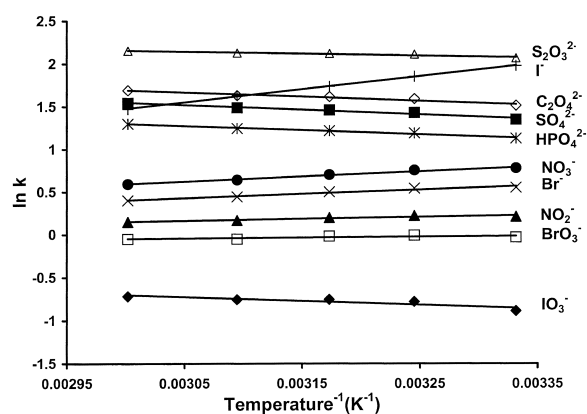


Fig. 2. Van't Hoff plots for anions separated on a Dionex AS14 column. A 3.5 m$M$ $CO_3^{2-}$–1 m$M$ $HCO_3^-$ eluent at 0.3 ml/min was used for the separation. The temperature range investigated was 27 to 60°C.

Table 1
Slopes, standard deviations, correlation coefficients and $P$ values from the van't Hoff plots of various anions[a]

| Anion | AS11 | | | AS14 | | |
|---|---|---|---|---|---|---|
| | Slope (K) | $r^2$ | $P$ value | Slope (K) | $r^2$ | $P$ value |
| Iodate | $-1300\pm300$ | 0.879 | 0.018 | $-200\pm200$ | 0.901 | 0.050 |
| Bromate | $-500\pm100$ | 0.942 | 0.006 | $190\pm20$ | 0.863 | 0.071 |
| Nitrite | $-400\pm100$ | 0.995 | 0.000 | $310\pm20$ | 0.987 | 0.007 |
| Bromide | $100\pm40$ | 0.898 | 0.014 | $590\pm20$ | 0.993 | 0.004 |
| Nitrate | $100\pm40$ | 0.898 | 0.014 | $670\pm10$ | 0.992 | 0.004 |
| Sulfate | $-2600\pm400$ | 0.999 | 0.000 | $-460\pm20$ | 0.988 | 0.006 |
| Oxalate | $-2500\pm300$ | 0.999 | 0.000 | $-400\pm90$ | 0.941 | 0.030 |
| Iodide | $1400\pm100$ | 0.997 | 0.000 | $1530\pm50$ | 0.998 | 0.001 |
| Thiosulfate | $-1700\pm200$ | 0.999 | 0.000 | $-170\pm30$ | 0.928 | 0.037 |
| Phosphate | $-1700\pm200$ | 0.998 | 0.001 | $-440\pm10$ | 0.987 | 0.007 |
| Thiocyanate | $1800\pm200$ | 0.999 | 0.000 | – | – | – |
| Perchlorate | $2000\pm200$ | 0.999 | 0.000 | – | – | – |

[a] Experimental conditions: anions were separated on a Dionex AS11 column using a 12 m$M$ hydroxide eluent at a flow-rate of 0.3 ml/min and a Dionex AS14 column using a 3.5 m$M$ $CO_3^{2-}$–1 m$M$ $HCO_3^-$ eluent at a flow-rate of 0.3 ml/min. A 2-μl injection was used. The van't Hoff plots covered a temperature range of 27 to 60°C. The standard deviations are those for the slopes obtained from three replicate runs and are not those for the regression.

anion-exchange columns studied herein. Regression parameters for the anions separated on both columns are presented in Table 1. While correlation coefficients are quoted in Table 1, they are poor measures of linearity. A better measure of the significance of a linear regression is the $P$ value. A $P$ value of less than 0.05 indicates a significant linear relationship at the 95% confidence level. Significant linear relationships were observed over the 27–60°C range for all anions studied, except iodate and bromate on the AS14. For these anions the $P$ value of the van't Hoff plots corresponded to the 90% confidence level. Thus, over the temperature range studied, van't Hoff plots on these ion-exchange columns can be considered linear.

A second characteristic of Figs. 1 and 2 is that the slopes of the van't Hoff plots are both negative and positive. In RPLC only exothermic behavior is observed [15,19–22]. That is, retention in RPLC always decreases with increasing temperature. However, in Figs. 1 and 2, both exothermic (decreasing retention with increasing temperature) and endothermic (increasing retention with increasing temperature) behavior is seen. That is, ion retention can either increase or decrease with increasing temperature. Similar behavior has been observed for cation-exchange [17] and anion-exchange on a Dionex AS-4A column [11].

It has been stated that the standard enthalpy changes for ion-exchange are small ($<2$ kcal/mol [23]; 1 cal$=4.184$ J). However, the slopes of the van't Hoff plot in Table 1 range from $-2600$ to $+2000$ K. In contrast the slopes of van't Hoff plots for organic nonelectrolytes in RPLC on carbon-coated zirconia are around $+1900$ K (calculated from van't Hoff plots in Ref. [19]) and about $+1200$ K on $C_{18}$ silica (Waters Delta Pak HPI) [24]. Thus, the temperature dependence can be as pronounced or more pronounced in ion chromatography than in RPLC. However, it is the range of the enthalpies of retention that is important in achieving selectivity changes. In RPLC the enthalpies of retention vary only 10–15% (calculated from van't Hoff plots in Refs. [19,24]). Much greater variation in enthalpy is evident in Table 1. Thus, as has been stated previously by Mao and Carr [19], temperature can have a much larger effect on the selectivity of electrolytes than nonelectrolytes. In the following sections, the experimental variables that affect the enthalpy of retention will be investigated, and some general trends in the temperature dependence of anion retention will be identified.

### 3.2. Effect of eluent on temperature dependence of retention

Fortier and Fritz noted that the temperature be-

Table 2
Slopes of van't Hoff plots for anions separated using different eluents[a]

| Anion | Slope (hydroxide) | Slope (carbonate) | $\Delta$ (slope) |
|---|---|---|---|
| Iodate | −1300 | 500 | 1800 |
| Bromate | −500 | 800 | 1300 |
| Nitrite | −400 | 700 | 1100 |
| Bromide | 100 | 1200 | 1100 |
| Nitrate | 100 | 1300 | 1200 |
| Sulfate | −2600 | −200 | 2400 |
| Oxalate | −2500 | −100 | 2400 |
| Iodide | 1400 | 2200 | 800 |
| Thiosulfate | −1700 | 700 | 2400 |
| Phosphate | −1700 | 300 | 2000 |
| Thiocyanate | 1800 | 2600 | 800 |
| Perchlorate | 2000 | 2800 | 800 |

[a] Experimental conditions: anions were separated on a Dionex AS11 column using a 12 m$M$ hydroxide eluent and a 7 m$M$ $CO_3^{2-}$–1 m$M$ $HCO_3^{-}$ eluent. A flow-rate of 0.3 ml/min was used. Injection volume was 2 μl. The slopes were determined over a temperature range of 27 to 60°C.

havior of cations changed with the eluent type [17]. Herein, the effect of temperature on retention was studied on an AS11 column using 12 m$M$ hydroxide and 7 m$M$ carbonate–1 m$M$ hydrogen carbonate. These eluents yielded comparable retention at 27°C. Table 2 shows the temperature dependence in terms of the slopes of the van't Hoff plots for various anions using these two eluents. Significant differences in the temperature dependence of retention are evident upon changing the eluent. In Table 2, shifting from a hydroxide to a carbonate eluent caused all of the slopes to become larger (more positive). That is, the exchange enthalpies became

more exothermic. For anions such as perchlorate and thiocyanate that displayed exothermic behavior with hydroxide, their retention decreased more dramatically with increasing temperature when a carbonate eluent was used. In contrast, anions such as phosphate and thiosulfate which displayed endothermic behavior with hydroxide (increasing retention with increasing temperature) became weakly exothermic with carbonate. In other words, their retention now decreases with an increase in temperature.

The temperature dependence of anion retention on an AS14 column was also studied for a 32 m$M$ hydroxide eluent instead of a 1 m$M$ hydrogen carbonate–3.5 m$M$ carbonate eluent (data not shown). These eluents also yielded comparable retention at 27°C. Changes in the temperature dependence of anion retention were also seen on the AS14 column when the eluent was changed. In this case, the temperature behavior of the weakly retained singly charged anions did not change. However, the temperature behavior of anions such as sulfate and oxalate became less endothermic and thiosulfate became completely exothermic.

The temperature dependence of retention for anions separated on the AS11 column with a 12 m$M$ hydroxide and a 32 m$M$ hydroxide eluent is given in Table 3. The 32 m$M$ hydroxide eluent produced smaller (more negative) slopes for the van't Hoff plots of all anions than the 12 m$M$ hydroxide eluent. Therefore, temperature behavior is a function of both the eluent type and the eluent concentration. However, as can be seen by comparing Tables 2 and 3, the effect of eluent type is more significant than the effect of eluent concentration.

Table 3
Changes in the slopes of the van't Hoff plots of anions caused by an increase in eluent concentration[a]

| Anion | Slope (12 m$M$ hydroxide) | Slope (32 m$M$ hydroxide) | $\Delta$ (slope) |
|---|---|---|---|
| Nitrate | 100 | 100 | 0 |
| Sulfate | −2600 | −3100 | −500 |
| Oxalate | −2500 | −3000 | −500 |
| Iodide | 1400 | 1200 | −200 |
| Thiosulfate | −1700 | −1900 | −200 |
| Phosphate | −1700 | −2800 | −1100 |
| Thiocyanate | 1800 | 1500 | −300 |
| Perchlorate | 2000 | 1800 | −200 |

[a] Experimental conditions: separations were performed on a Dionex AS11 column with 12 m$M$ and 32 m$M$ hydroxide as eluent at a flow-rate of 0.3 ml/min. A 2-μl injection was used. Slopes were determined over a temperature range of 27 to 60°C.

## 3.3. Effect of stationary phase on temperature dependence of retention

To investigate the effect of the stationary phase on the temperature behavior of retention, a 32 m$M$ hydroxide eluent was used with both the AS11 and the AS14 column. Table 4 gives the temperature dependences observed for each column. In general retention on the AS14 column is more exothermic than that on the AS11 column. That is, anions such as nitrate whose temperature behavior is weakly exothermic on the AS11 column, becomes more exothermic on the AS14 column. Phosphate shows strongly endothermic behavior on the AS11 column, but almost no temperature dependence on its retention on the AS14 column.

In comparing Tables 2 and 4, changing the column type has less effect on the temperature dependence of singly charged anions than does changing the eluent type. However, for multiply charged anions the effect of column type on temperature dependence is greater than that of eluent type. Therefore, the stationary phase has a significant effect on the temperature behavior of anions, and one that is different from that of eluent type.

## 3.4. Effect of temperature on selectivity

The van't Hoff plots in Figs. 1 and 2 reveal that temperature significantly affects the selectivity of an ion-exchange separation. Therefore, temperature can be used as an aid in method development. Moreover, if a model were available that can explain (or

Table 4
Comparison of the slopes of van't Hoff plots on Dionex AS11 and AS14 columns[a]

| Anion | Slope (AS11) | Slope (AS14) | $\Delta$ (slope) |
|---|---|---|---|
| Nitrate | 100 | 700 | 600 |
| Iodide | 1200 | 1600 | 400 |
| Sulfate | −3100 | −400 | 2700 |
| Oxalate | −3000 | −300 | 2700 |
| Phosphate | −2800 | 0 | 2800 |
| Thiosulfate | −1900 | 800 | 2700 |

[a] Experimental conditions: separations were performed on each column with 32 m$M$ hydroxide as eluent at a flow-rate of 0.3 ml/min. A 2-µl injection was used. Slopes were determined over a temperature range of 27 to 60°C.

predict) the effect of temperature on selectivity, it would greatly facilitate method development. A previously cited model for ion-exchange [17,23], which is only valid for qualitative discussions, is:

$$\ln K_B^A = \frac{\Pi}{RT} \cdot (|z_A| \nu_B^* - |z_B| \nu_A^*) \qquad (3)$$

where $K_B^A$ is the selectivity coefficient of A over B, $\Pi$ is the swelling pressure, $z_A$ is the charge on ion A, $z_B$ is the charge on ion B, and $\nu_A^*$ and $\nu_B^*$ are the molar solvated volumes for ions A and B, respectively. According to Eq. (3), the retention of ion A increases directly with swelling pressure or charge, whereas it decreases with an increase in molar solvated volume. Gregor and Bregman went further and proposed that changes in the selectivity coefficient as a function of temperature can be accounted for through the $(|z_A| \nu_B^* - |z_B| \nu_A^*)$ term [25]. In other words, selectivity changes are caused by differences in the relative hydration of ions A and B as the temperature is varied. Unfortunately this approach requires values of molar solvated volume at different temperatures. Such values are not readily available. Consequently, this approach is useful only on a qualitative basis (as was used by Gregor and Bregman [25]) for understanding the effect of temperature on selectivity, and reliable predictions cannot be made.

Although the effect of temperature on the retention of a particular anion cannot be predicted, a number of features can be extracted from the van't Hoff plots. Based on these features, conclusions can be made as to what effect temperature may have on the selectivity between specific anions. In Figs. 1 and 2, three groups of behavior are evident. These groupings are summarized in Table 5. Within a group the temperature behaviors are approximately the same, as evidenced by the more or less parallel lines in Figs. 1 and 2. Since the effect of temperature within a group is approximately the same, temperature has little effect on the selectivity between those anions. However, temperature can cause selectivity changes between anions from different groups. For example as shown in Fig. 3A, thiosulfate and phosphate (group 2) elute before thiocyanate (group 3) at 27°C. Increasing the column temperature (Fig. 3B) causes thiocyanate to be eluted before thiosulfate and phosphate, without affecting the selectivity between

Table 5
Groups of anions showing similar temperature behavior

| Group | Group name | Examples | Characteristics |
|---|---|---|---|
| 1 | Weakly retained anions | Iodate, bromate, nitrite, bromide and nitrate | Retention increases or decreases with increasing temperature |
| 2 | Multiply charged anions | Sulfate, oxalate, phosphate and thiosulfate | Retention significantly increases with increasing temperature |
| 3 | Strongly retained singly charged anions | Iodide, thiocyanate and perchlorate | Retention significantly decreases with increasing temperature |

thiosulfate and phosphate. This illustrates that temperature can be used to tailor the selectivity of a separation.

Similar group behavior is evident in the temperature dependence of anions on the AS11 column with 32 m$M$ hydroxide. Fig. 4 shows chromatograms

obtained at 27 and 60°C. Although the retention of the group 3 anions (iodide, thiocyanate, perchlorate) decreased dramatically with temperature, there is no change in selectivity between these anions. Further, the selectivity between anions in group 2 stayed the same. However, the selectivity of the group 2 anions (sulfate, oxalate, phosphate, thiosulfate) changed with respect to nitrate (group 1). It is apparent that
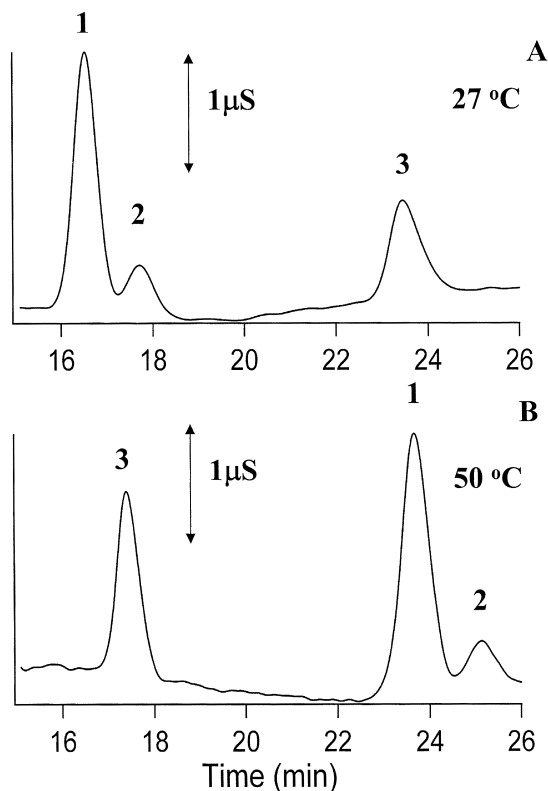


Fig. 3. Changes in selectivity caused by increased temperature. The separation was performed on a Dionex AS11 column using 12 m$M$ hydroxide at 0.3 ml/min. A 2-µl injection was used. 1= Thiosulfate, 2=phosphate, 3=thiocyanate.
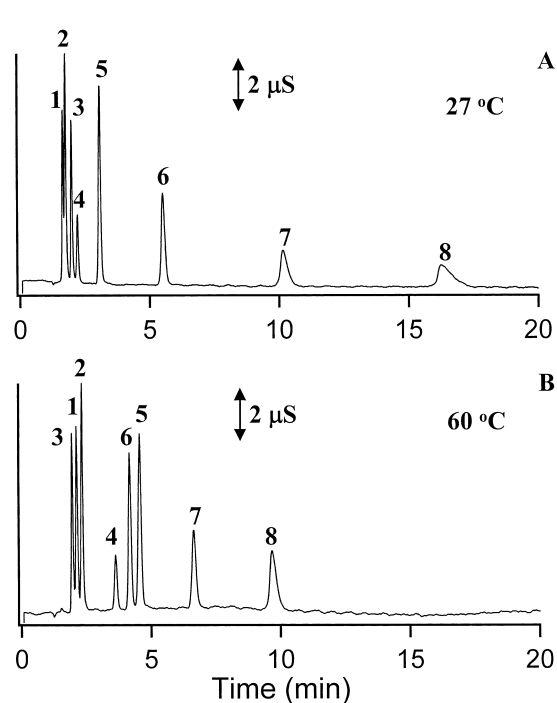


Fig. 4. Elution order changes caused by increased temperature. The separation was performed on a Dionex AS11 column using a 32 m$M$ hydroxide eluent. The flow-rate was 0.3 ml/min. A 2-µl injection was used. 1=Sulfate, 2=oxalate, 3=nitrate, 4=phosphate, 5=thiosulfate, 6=iodide, 7=thiocyanate, 8=perchlorate.

Table 6
The effect of temperature on efficiency and peak asymmetry[a]

| Anion | Efficiency | | Peak asymmetry | |
|---|---|---|---|---|
| | 27°C | 60°C | 27°C | 60°C |
| Sulfate | 5800 | 7400 | 0.85 | 0.94 |
| Iodide | 6900 | 8300 | 1.58 | 1.13 |
| Thiosulfate | 6600 | 7500 | 0.86 | 1.03 |
| Thiocyanate | 5600 | 7700 | 3.07 | 1.41 |
| Perchlorate | 4000 | 6300 | 3.33 | 1.66 |

[a] Experimental conditions: Dionex AS11 column with 32 m$M$ hydroxide as eluent at a flow-rate of 0.3 ml/min. A 2-µl injection was used.

group-wise changes in elution order can be obtained by raising the column temperature.

### 3.5. Changes in efficiency and peak asymmetry as a function of temperature

Many groups have reported that increasing the temperature of a column helps improve peak shape and efficiency [4,18,26]. This is attributed to improved mass transfer. However, it was not clear that a significant improvement would be observed for the agglomerated stationary phases used herein. Table 6 shows the efficiency for various analytes at different temperatures. The efficiency improved for all anions upon increasing the column temperature. These improvements ranged from 13% for thiosulfate to 58% for perchlorate. Further, the symmetry of all anion peaks improved, particularly that of the thiocyanate and perchlorate peaks.

## 4. Conclusion

This study explored the effect of temperature on the retention factors of various inorganic anions on two commercially available ion chromatography columns. Retention in ion chromatography can be an endothermic or exothermic process. Thus significant selectivity changes can be achieved by varying the column temperature. However, the anions studied were found to behave in groupings of behavior. Namely, weakly retained singly charged anions behaved as one group, multiply charged anions behaved as another group, and the strongly retained singly charged anions behaved as yet another group.

Altering the column temperature failed to change the selectivity of anions within a group. However, selectivity changes were seen for anions in different groups, reversing the elution order in some cases. Thus, column temperature can be an effective variable to alter ion chromatographic selectivity in selected cases.

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