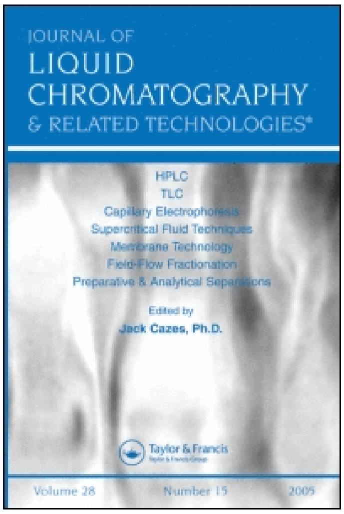

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EFFECTS OF HIGH CONCENTRATION OF CHLORIDE ON THE DETERMINATION OF TRACE ANIONS BY ION CHROMATOGRAPHY

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ABSTRACT

Using both UV-Vis and conductivity detectors, the effects of high concentration of chloride on the determination of trace anions were studied on three different analytical columns by ion chromatography. The variations of retention behavior of these anions were caused by self-elution effect and on-column eluent change in the presence of high concentration of chloride. As the chloride concentration increased, linear ranges of the other anions became narrow. The anions separated on the column, which had higher capacity and had wider linear ranges. When their peaks overlapped with chloride, the deviations of weak acid anions were caused by anion-proton interactions within the suppressor. However, the other weak acid anions, which could not overlap with chloride and the strong acids anions, were not affected. In this paper, accurately quantitative analysis methods and their linear ranges were determined.

INTRODUCTION

The determination of ionic species in solution was a classical analytical problem with a variety of solutions. Since ion chromatography (IC) was invented in 1975, it has became the workhorse laboratory instrument for the determination of anions.[1,2] In most environmental water samples analyzed by IC, the concentration of anions were within an order of magnitude of each other and these anions could be determined with good accuracy. However, this was not the case when determining trace concentration of anions in the presence of large concentration of matrix ions. In these instances, although the anions were well separated and had sharp peaks, IC might produce inaccurate results. Byumn et al.[3] were the first to investigate the response of a small concentration of sulfate in the presence of large concentration of chloride. The determination of 0-100 mg L^{-1} of sulfate in the presence of 8000 mg L^{-1} or higher chloride was unreliable. Smith[4] reported that retention time and the peak height of 31.2 mg L^{-1} chloride in the presence of sulfuric acid, equivalent to 0 to 12200 mg L^{-1} sulfate, increased with increasing concentration of sulfured acid. The peak height of 12.5 mg L^{-1} chloride was also increased due to the presence of 0.8 mol L^{-1} sodium hydroxide.

Tan et al.[5] studied the effect of the concentration of common anions on the determination of $HAsO_4^{2-}$. The change in the arsenate peak height might have occurred due to the competition between the arsenate and other anions for the active sites on the resin in analytical columns during the exchange with eluent anions. Singh et al.[6,7] studied the effect of the concentration of common anions on the determination of several anions. Although, their peaks were reasonably sharp and well resolved up to the baseline in the high concentration of matrices, they had serious effects on the weak acids anions.

Cox et al.[8] found the deviation was not caused by overloading of the analytical column. Singh et al.[6] found that it was the cation which caused a reduction in the peak height of weak acid anions when relatively large concentrations of cations were present in the analyte matrix. Novic et al.[9] studied the influence of the sample matrix composition on the accuracy of the ion chromatographic determination of anions.

In this paper, the effects of high concentration of chloride on the retention, separation and quantitative analysis of the other trace anions have been systematically studied on three analytical columns, which had different properties. Accurate quantitative analysis methods and their linear ranges were determined in the presence of high concentration of chloride. Some special test phenomena were investigated from their separation mechanism.

EXPERIMENTAL

Instrumentation

Chromatographic analyses were performed on a metal-free Dionex DX-300 ion chromatography (Dionex Corp., Sunnyvale, CA, U.S.A) equipped with an advanced gradient pump, an ASRS II self regenerating suppressor (4 mm, Dionex), a 50 μL injection loop, a Dionex variable wavelength detector, and a conductivity detector.

The analytical columns were an IonPac AS4A-SC (250×4 mm, I.D.) protected by an IonPac AG4A-SC(50×4 mm, I.D.) Guard column, an IonPac AS11-HC (250×4 mm, I.D.) protected by an IonPac AG11-HC(50×4 mm, I.D.) Guard column, and an IonPac AS14 (250×4 mm, I.D.) protected by an IonPac AG 14(50×4 mm, I.D.) Guard column.

Data collection and operation of all components in the system were controlled by Dionex AI-450 chromatographic software interfaced via an ACI-2 advanced computer interface to an AST Power Premium 3/33 computer.

The eluent flow-rate was 1.0 mL min^{-1}. All measurements were made at room temperature.

Chemicals and Reagents

All reagents were of analytical-reagent grade. Stock standard solutions of F^-, Cl^-, Br^-, NO_3^-, NO_2^-, SO_4^{2-}, and HPO_4^{2-} (1000 mg L^{-1}) were prepared by dissolving appropriate salts in 1 L of deioned water. A series of working standard F^-, Cl^-, Br^-, NO_3^-, NO_2^-, SO_4^{2-}, and HPO_4^{2-} solutions were prepared by appropriate dilution of the stock standard solutions.

RESULTS AND DISCUSSION

In this paper, three anion analytical columns with different capacities were chosen to evaluate anions assay. Their structural and technical characteristics were summarized in Table 1. It was seen that AS4A-SC and AS11-HC columns had the same functional group. But, their hydrophilicities and column capacities were different. Among the three columns, AS11-HC column had the biggest capacity and the highest hydrophilicity. AS14 column had medium capacity, but, its hydrophobicity was the highest. The best elution compositions for the three columns were listed as follows:

AS4A-SC 3.15 mmol L^{-1} Na_2CO_3 / 0.9 mmol L^{-1} $NaHCO_3$

Table 1

Structural and Technical Properties of Three Analytical Columns

Column	Particle Diameter (μm)	Substrate %X Linking	Capacity (μeq col^{-1})	Functional Group	Hydrophobicity
AS4A-SC	13	55	20	Alkanol QA	Medium-low
AS14	9	55	65	Alkyl QA	Medium-high
AS11-HC	13	55	225	Alkanol QA	Low

QA: Quaternary ammonium.

AS11-HC 20 mmol L^{-1} NaOH

AS14 1.8 mmol L^{-1} Na_2CO_3 / 1.7 mmol L^{-1} $NaHCO_3$

Since the common anions had high hydrophilicity, they had strong affinity with AS 4A-SC column. Although AS 14 column had higher hydrophobicity and column capacity than AS 4A-SC column, its elution strength needed for best separation was lower.

The conductivity detector and UV-Vis detector set at 215 nm were placed in series. Two chromatograms of anions could be gotten simultaneously. When high concentrations of chloride was present in the sample, its peak would be partly or completely overlapped with NO_2^- peak. This would result NO_2^- could not be detected by the conductivity detector. Since chloride had no UV absorbance at 215 nm, Br^-, NO_2^-, and NO_3^- had strong UV absorbance at this wavelength, it was suitable for the analysis of Br^-, NO_2^-, and NO_3^- by using a UV-Vis detector. F^-, SO_4^{2-}, and HPO_4^{2-} did not overlap with chloride and could be detected by a conductivity detector.

The connected order of these two detectors was very important. A conductivity detector must be connected in advance. After passing through the suppressor, the eluents were suppressed to H_2O (AS11-HC column used) or H_2CO_3 (AS4A-SC or AS14 column used), which had almost the same UV absorbance as chloride. When a high concentration of chloride was eluted out from the analytical column, it did not produce a detection signal in the UV chromatogram (shown in Figure 1 [a]). But, NO_2^- could produce a detection signal. NO_2^- was well separated and could be accurately quantitated. If a UV-Vis detector was connected in advance, the eluents could not be suppressed before they entered the UV-Vis detector. Since the UV absorbance of the eluent was higher than that of chloride, chloride produced an inverted peak. When

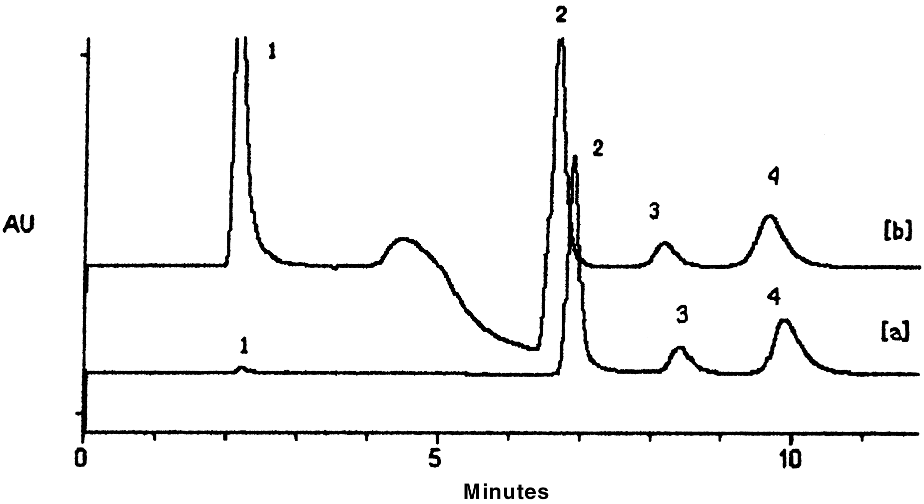

Figure 1. Chromatograms of three anions in the presence of 4500 ppm Cl^- with UV-Vis detector on AS14 column. A) conductivity detector contacted first; b) UV-Vis detector contacted first; 1) System peak; 2) NO_2^-; 3) Br^-; 4) NO_s^-.

NO_2^- was eluted with a high concentration of chloride from an analytical column, the high concentration of chloride would produce a large inverted peak, which interfered with NO_2^- peak (shown in Figure 1 [b]). NO_2^- could not be accurately quantitated. Figure 1 [a] and [b] were the chromatograms of three anions separated on an AS14 column in the presence of 4500 ppm Cl^- detected by a UV-Vis detector. The connecting order of the two detectors was different and the UV chromatograms were different for the two connection modes.

Effect of Chloride on the Retention Behavior of Anions

As the chloride concentration increased, the retention time of NO_2^- and Br^- increased and finally overlapped with NO_3^- (shown in Figure 2). This could not be explained by taking into account the self-elution effect.[11] The self-eluent effect of anions prevented other anions from being retained by the stationary phase. This process continued until the sample plug was diluted enough by the eluent, so that the anions were retained. As a result of this process, shorter retention time was expected. Regardless of the partial chloride retention by the stationary phase, there might be another additional retention / elution mechanism. When the high concentration of chloride passed through the column, the

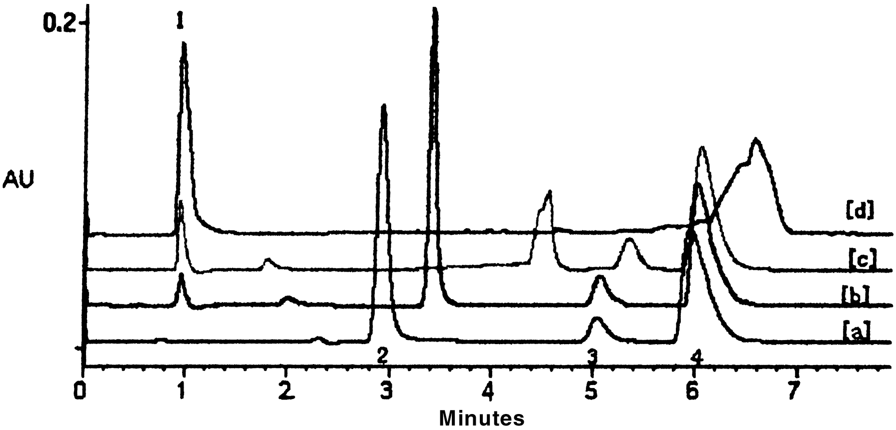

Figure 2. Effect of Cl^- concentration on the retention time of NO_2^-, Br^-, and NO_3^- with UV-Vis detector on AS4A-SC column. a) 150 ppm Cl^-; b) 4050 ppm Cl^-; c) 12000 ppm Cl^-; d) 36450 ppm Cl^-; 1) System peak; 2) NO_2^-; 3) Br^-; 4) NO_3^-.

stationary phase was converted mostly to the chloride form. The anions could be eluted out for a certain period of time with the eluent enriched with chloride. This phenomena was called on-column change of the eluent.[9] The strength of this part of the eluent was weaker than that of the original eluent and removed faster than NO_2^-, Br^-, and NO_3^-. So, NO_2^-, Br^- and NO_3^- had longer retention time in the presence of high concentrations of chloride.

In general, the anions were eluted by both self-elution effect and on-column change of the eluent. The former had only a little fraction of the time during which the sample plug passed through the column. When the Cl^- concentration was more than 36450 ppm, NO_2^- and NO_3^- were eluted together. This phenomenon could also be seen in Figure 4. Since the AS11-HC column had a higher capacity than the AS 4A-SC column, it has less effect. The higher the column capacity, the less effect there was. In this paper, the degree of effect was AS4A-SC > AS14 > AS11-HC.

When the high concentration of SO_4^{2-} passed through the column, all the elution times of NO_2^-, Br^-, and NO_3^- were decreased (shown in Figure 3). As it was eluted later than NO_2^-, Br^-, and NO_3^-, on-column eluent change could not affect the retention behavior of NO_2^-, Br^-, and NO_3^-. Their retention time was affected only by the self-elution effect of SO_4^{2-}.

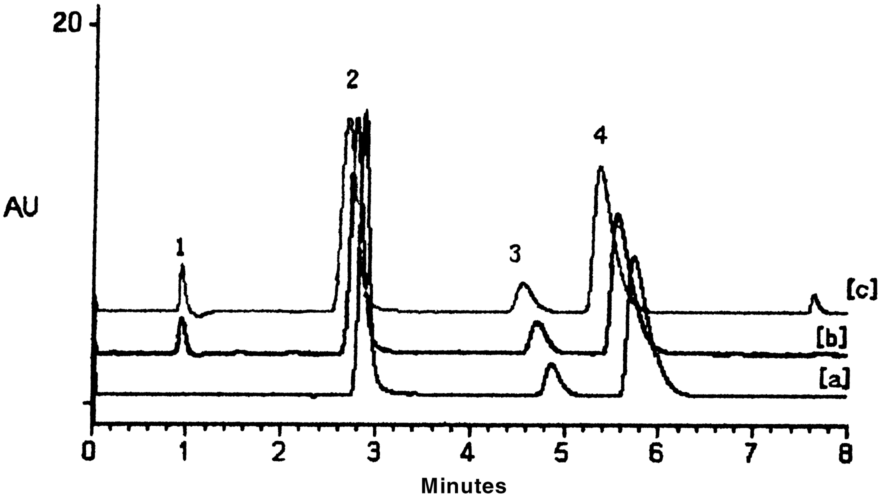

Figure 3. Effect of SO_4^{2-} concentration on the retention time of NO_2^-, Br^-, and NO_3^- with UV-Vis detector on AS4A-SC column. a) 20 ppm SO_4^{2-}; b) 4050 ppm SO_4^{2-}; c) 9100 ppm SO_4^{2-}; 1) System peak; 2) NO_2^-; 3) Br^-; 4) NO_3^-.

Effect of High Concentration of Chloride on the Quantitative Analyses of Anions

When the high concentration of chlorides was present, its peak would partly or completely overlap with the NO_2^- peak. As the chloride concentration increased (AS14 > 4050 ppm, AS4A-SC > 4050 ppm, AS11-HC > 9100 ppm), the peak area and height of NO_2^- would gradually be decreased. But, the peak areas of Br^- and NO_3^- did not change, their peak heights had a little change.

The suppressor could exchange all the influent cations for H^+. In doing so, it reduced the eluent background to that of weakly conduction H_2CO_3 or H_2O and converted the common anions such as Cl^-, Br^-, and SO_4^{2-} to strongly ionized acids. The cations in eluents could be completely and speedily exchanged for H^+ at the surface of the suppressor. When the high concentration of chloride passed through the suppressor, a significant accumulation of H^+ ions occurred on the surface of the suppressor during the ion-exchange process.[12] The accumulation of H^+ ions would cause the formation of the HNO_2 ion pair after reaction with NO_2^-. The formation of HNO_2 would cause a decrease in the UV absorbance. It had been proven that the UV absorbance of HNO_2 was higher than that of NO_2^- at 215 nm. In addition, the process of proton-nitrite association might result in broadening of the NO_2^- peak. But, the accumulation of H^+

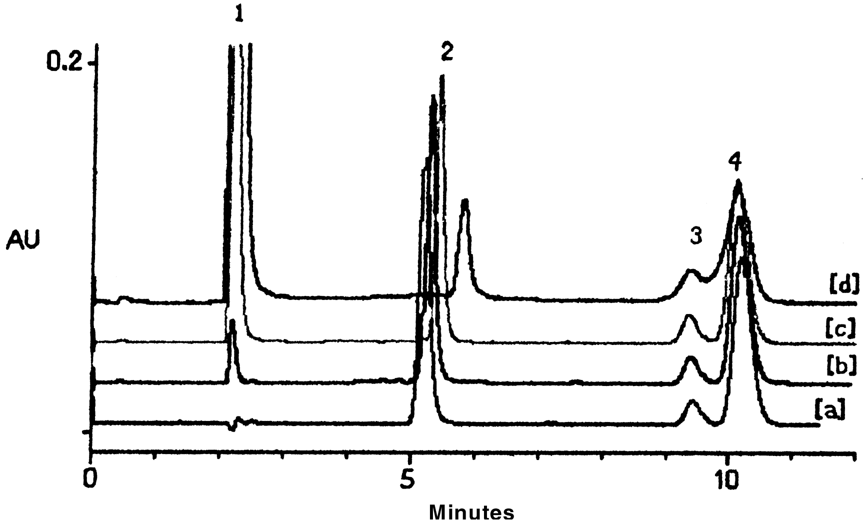

Figure 4. Effect of Cl^- concentration on the NO_2^-, Br^-, and NO_3^- with UV-Vis detector on AS11-HC column. a) 6 ppm Cl^-; b) 4050 ppm Cl^-; c) 12150 ppm Cl^-; d) 36450 ppm Cl^-; 1) System peak; 2) NO_2^-; 3) Br^-; 4) NO_3^-.

ions would be eluted quickly; there is no effect on the peak areas of other anions which do not overlap with chloride. Since Br^- and NO_3^- were strong acid anions, there were no effects on their peak areas. Their peak heights had little change because of self-elution and the band-compression effects. The effect of Cl^- concentration on the NO_2^-, Br^-, and NO_3^- on an AS11-HC column was shown in Figure 4.

When the high concentration of SO_4^{2-} was present, SO_4^{2-} was eluted later than NO_2^-, Br^-, and NO_3^-. NO_2^-, Br^-, and NO_3^- could not be overlapped with SO_4^{2-}. Thus, their peak areas could not be affected.

To confirm this, a certain amount of chloride, whose peak overlapped with NO_2^- peak partly to completely, was loaded on the analytical column in advance. This avoided a self-elution effect. As the Cl^- concentration increased, its peak overlapped with NO_2^- peak and its peak height and area decreased gradually. Although the decreased ranges on the three analytical columns were different (detected by a conductivity detector), all of them finally had a certain values (AS 4A-SC 32.9% decrease, AS 14 36.6% decrease, AS 11-HC 41.3% decrease). Because the concentration of H^+ ions came to its maximum, the fraction of HNO_2 produced on the suppressor did not change.

Table 2

Effect on the Peak Height and Area of NO_2^- in Different Matrices on AS14 Column

		LiCl	NaCl	KCl	$MgCl_2$	$SrCl_2$
4000 ppm Cl^-	Peak height	9892	9944	9781	10167	10212
	Peak area	131722	130188	130577	132245	131429
8100 ppm Cl^1	Peak height	10172	10077	10301	10640	10962
	Peak area	106723	105061	104876	107255	102429
12000 ppm Cl^-	Peak height	9386	9307	9266	9565	9489
	Peak area	89061	84712	84130	88676	89512

At the suppressor, the cation was exchanged by H^+ completely and quickly. We tested LiCl, NaCl, KCl, $MgCl_2$ and $SrCl_2$ as the matrices at the same chloride concentration. It could be seen in Table 2 that all of these matrices had almost the same effects on the peak height and area of NO_2^-. But, the results had little difference,[10] so it was considered that the higher valence of cation had a higher effect.

When the sample entered the analytical column, all the cations in samples could not be retained and displaced by the elution cation. They were eluted from the column quickly and produced a big peak at the system peak. Thus, all kinds of cations had the same results.

Quantitative Analysis of Anions

Among the three analytical columns, the AS14 column was the best column to separate F^-. F^- peak and the inverted system peak could be well separated. But, as the Cl^- concentration increased, more and more elution cations were eluted at the dead time. They produced a large conductivity signal. This would result in the system inverted peak turning into a positive peak and overlapping gradually with the F^- peak. F^- could not be determined. This was shown in Figure 5.

The linear ranges of other anions would changed with the variation of Cl^- concentration presented in samples. The higher concentration of Cl^- would result in narrower linear ranges. On the other hand, when the Cl^- concentration was constant, each anion had different linear ranges on the three analytical

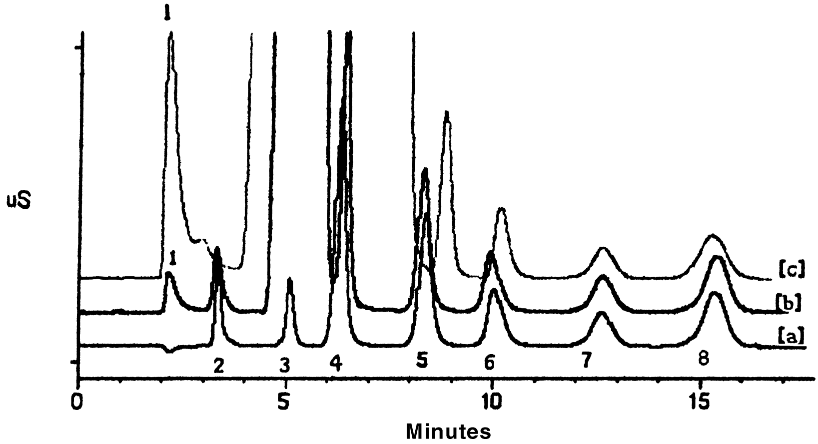

Figure 5. Effect of chloride concentration on the quantitative analysis of F^- with conductivity detector on AS14 column. a) 6 ppm Cl^-; b) 1350 ppm Cl^-; c) 13150 ppm Cl^-; 1) System peak; 2) F^-; 3) Cl^-; 4) Br^-; 5) NO_3^-; 6) NO_2^-; 7) SO_4^{2-}; 8) HPO_4^{2-}.

columns. The column, which had the higher capacity, had the wider linear range. This could be seen in Table 3. Thus, when the sample had trace anions and high concentration of chloride, the column which had a higher capacity should be considered first.

Table 3

Linear Range of each Anion in the Presence of Different Cl^- Concentrations

	Cl^- (ppm)	NO_2^- (ppm)	Br^- (ppm)	NO_3^- (ppm)
AS4A-SC	6	0.4 ~ 50	0.8 ~ 50	0.35 ~ 45
	4000	0.4 ~ 50	0.8 ~ 50	0.35 ~ 45
	12000	0.4 ~ 25	0.8 ~ 25	0.35 ~ 22.5
AS 14	6	0.4 ~ 100	0.8 ~ 200	0.35 ~ 90
	4000	0.4 ~ 50	0.8 ~ 100	0.35 ~ 90
	12000	0.4 ~ 25	0.8 ~ 50	0.35 ~ 45
AS 11-HC	6	0.4 ~ 100	0.8 ~ 200	0.35 ~ 180
	4000	0.4 ~ 50	0.8 ~ 100	0.35 ~ 180
	12000	0.4 ~ 50	0.8 ~ 200	0.35 ~ 90

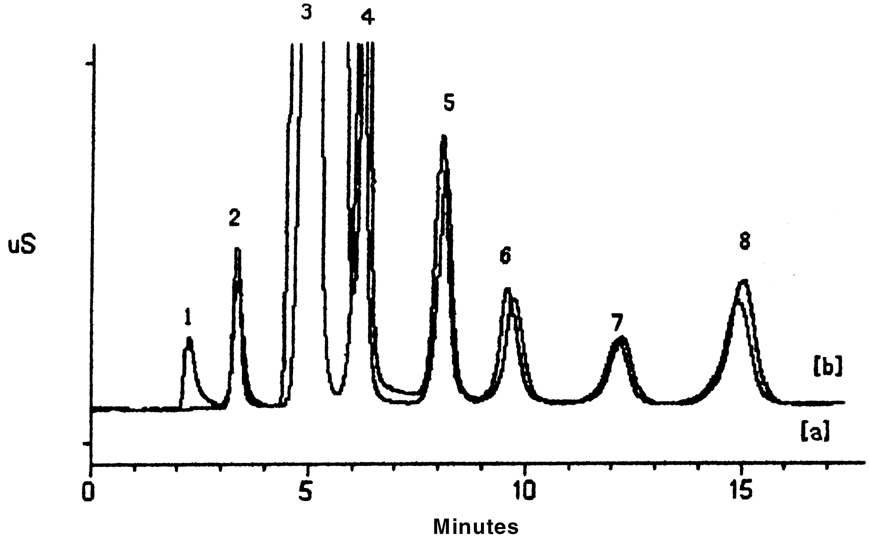

Figure 6. Effect of high concentration of chloride on the peak height with UV-Vis detector on AS14 column. a) 150 ppm Cl^-; b) 1350 ppm Cl^-; 1) System peak; 2) F^-; 3) Cl^-; 4) Br^-; 5) NO_3^-; 6) NO_2^-; 7) SO_4^{2-}; 8) HPO_4^{2-}.

Figure 6 was the effect of high concentration of chloride on the peak height on an AS14 column with a conductivity detector. It was seen that the peak height of F^-, NO_3^-, NO_2^-, SO_4^{2-}, and HPO_4^{2-} had little change while the chloride concentration increased. This was possible, because a high concentration of chloride could overload the separator column, by occupying all or most of the exchange sites on the column. The overloading of the column would result in a broadening or asymmetry in the anion peaks. However, the possibility of overloading of the column due to a large concentration of chloride was ruled out. If it occurred, it should affect the SO_4^{2-} peak more than the HPO_4^{2-} peak, because SO_4^{2-} eluted before HPO_4^{2-} and, therefore, had less affinity for the column than HPO_4^{2-}. On the basis of the explanation and experimental observations presented in Figure 6, we suspected that the ion chromatographic determination of anions in the presence of a very high concentration of chloride, was not affected by overloading the column, but by self-elution and band-compression effects. However, their peak areas almost did not change.

Thus, its linear range of chloride was wider than that of peak height. But, quantitative analysis by peak height was the routine method in the laboratory. Table 4 listed the maximum chloride concentration at which the deviation was less than 10%.

Table 4

Maximum Chloride Concentration Allowed*

		F^{-}[a]	NO_2^{-}[a]	Br^{-}[a]	NO_3^{-}[a]	HPO_4^{2-}[a]	SO_4^{2-}[a]
AS4A-SC	CD	150	200	1300	12000	4000	4000
	UV	/	450	800	1300	/	/
AS11A-HC	CD	450	4050	12000	4000	/	4000
	UV	/	4050	12000	4000	/	/
AS14A	CD	900	450	1300	4000	12000	4000
	UV	/	450	800	1300	/	/

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* Deviation less than 10%. [a] ppm CD: conductivity detector.

CONCLUSION

In general, the high concentration of chloride had a serious effect on the determination trace anions. Thus, standard addition was recommended for the determination of anions in samples containing large mounts of chloride, where they might be determined by the use of a calibration.

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