Determination of anions in certified reference materials by ion chromatography[1]

Joung Hae Lee[a],*, Jong Seung Kim[b], Byung Hoon Min[c], Sun Tae Kim[c], Jong Hun Kim[d]

[a]*Korea Research Institute of Standards and Science, Taejon 305-600, South Korea*
[b]*Department of Chemistry, Konyang University, Nonsan 320-711, South Korea*
[c]*Department of Environmental Engineering, Taejon University, Taejon 300-716, South Korea*
[d]*Department of Science and Technology, Jeonju University, Jeonju 560-759, South Korea*

Abstract

Certified reference materials (CRMs) which can be used to analyze anions in aqueous solution were prepared. Using ion chromatography, highly concentrated CRM solutions containing seven different anions (F^-, Cl^-, NO_2^-, NO_3^-, Br^-, PO_4^{3-}, and SO_4^{2-}, 100 mg kg^{-1} each) could be directly separated without making any diluted solutions. To obtain optimized separation conditions in this highly concentrated sample solution, a number of experiments including change of eluent composition and flow-rate of the eluents and injection volumes were attempted. The best results were observed when a mixture of 2.0 mM Na_2CO_3 and 2.5 mM $NaHCO_3$ as an eluent was used with conditions of 0.5 ml min^{-1} as flow-rate and a 5 μl sample loop. The resolution value reached to 1.5, which is sufficient for quantitative analysis and all of seven different anions were perfectly separated within 15 min. © 1998 Elsevier Science B.V. All rights reserved.

Keywords: Inorganic anions

1. Introduction

Ion chromatography (IC) developed by Small et al. in 1975 [1] has so far been used in the analysis of cations and anions present in inorganic or organic materials. As the technique allows for the realtime solving of such problems as analysis limitation and time wasting etc., during the actual experiment, it has been widely used instead of wet analysis techniques such as titrimetry, spectrometry, argentometry, and colorimetry. In addition, IC has been rapidly embraced due to development of hardware manipulation such as the development of highly qualified and specialised ion-exchange resins.

Presently, IC finds general application in power plant, semiconductor, detergent, medicine, food, agricultural, pulp manufacturing, mining and metal industries, and more importantly in the environmental field [2,3]. Thus, it has been certified and adopted by Korean Standard in South Korea [4], the American Society for Testing and Materials (ASTM) and the US Environmental Protection Agency (EPA) [5] in the USA.

Certified reference materials (CRMs) are commercially produced as a highly concentrated solutions (100 or 1000 mg kg^{-1}) to maintain solution stability

[6]. IC is normally used for analyzing low concentration samples, below 10 mg kg^{-1} [7–10]. In other words, the direct measurement of highly concentrated solution like commercialized CRMs without any dilution process results in a poor resolution in ion chromatography. Using ion chromatography, only a few studies for the measurement of ion concentrations above 100 mg kg^{-1} have been done [11]. Therefore, in this study, we developed a method which is able to provide a convenient resolution in an ion chromatogram upon changing the composition and flow-rate of the eluents, and the injection volume of samples, when a highly concentrated solution (100 mg kg^{-1}) is used. A CRM composed of a highly concentrated mixture containing seven different ions (F$^-$, Cl$^-$, N$_2^-$, NO$_3^-$, Br$^-$, PO$_4^{3-}$, and SO$_4^{2-}$) was prepared. The ions were completely separated by IC to which developed analytical methods were applied.

2. Experimental

2.1. Instrumentation

In this study, analysis and data collection were performed by PeakNet 4.3 Software using a DX 500 ion chromatograph purchased from Dionex. An AS40 Automated Sampler was used for the injection of samples. As a separator column, AS4A-SC, used in most laboratories in the world, was purchased from Dionex as well. Eluent compositions are well known as one of the most important factors in ion separation. Therefore, variations of eluents mainly composed of NaHCO$_3$, Na$_2$CO$_3$, and NaOH are carried out to reach an optimum separation condition.

Before analyzing, gases dissolved in eluents should be eliminated because gases entering an eluent pump can decrease the stability of the eluent flow-rate, resulting in poor reproducibility on chromatograms. Also when gases enter a detector, noise peaks may appear in ion chromatograms. Helium gas is used to eliminate those other gases present in eluents.

The flow-rate of the eluent was initially fixed at 2 ml min^{-1} and gradually varied to obtain the optimum separation condition. Also, the sample loop

Table 1
Analytical conditions for ion chromatographic analysis

Chromatograph:	Dionex DX 500
Separator Column:	Ion Pac AG4A-SC/AS4A-SC
Eluent:	1.7 mM Na HCO$_3$ + 1.8 mM Na$_2$CO$_3$
	3.0 mM NaHCO$_3$ + 2.4 mM Na$_2$CO$_3$
	2.5 mM NaHCO$_3$ + 2.0 mM NaOH
Eluent flow-rate:	2.0, 1.1, 0.8, 0.5 ml min^{-1}
Sample loop:	20, 10, 5, μl
Detection:	Suppressed conductivity
Suppressor:	ASRS
Regenerant:	Water
Current:	50, 100 mA

was changed to control the injection volume. Detailed conditions of anion separation using ion chromatography are listed in Table 1.

2.2. Preparation of CRM

CRM was prepared as follows: highly purified chemicals purchased from chemical company were accurately weighed. They were dissolved and diluted with deionized water and finally measured by ion chromatography.

Considering the stability of the prepared CRM, we used polyethylene bottles for its storage. Most of the bottles were sunk in 10% HCl and 10% HNO$_3$ solution, respectively, for at least 24 h and then washed with deionized water several times. The deionized water was prepared through use of a Milli-Q instrument (resistance 18 MΩ cm), mixed bed tank, TD organex-Q to remove organic materials, and a membrane filter (Millipack-40 system). Finally, purified water was passed through a 0.22 μm filtration kit. In water purified by above method, the concentration of impurities was found to be below 5 ppb.

In spite of using highly purified chemical reagents, they were normally found to contain trace amounts of water, which can critically influence weight results. Detaile experimental conditions for the removal of the water are described in Table 2. After drying the samples in an oven at a suitable temperature to which they are stable, the samples were cooled down to room temperature for an appropriate period by storing in desiccator containing anhydrous magnesium perchlorate.

NaF 22.1009 g, NaCl 16.4848 g, Na$_2$SO$_4$ 14.7869

Table 2
Preparation conditions of high purity materials for CRM solution

Ion	High-Purity Material	Purity	Preparation condition
F^-	Sodium fluoride (NaF)	>99.99%	140°C, 24 h
Cl^-	Sodium chloride (NaCl)	>99.999%	600°C, 1 h
SO_4^{2-}	Sodium sulfate Anhydrous (Na$_2$SO$_4$)	>99.99%	105°C, 2 h
Br^-	Potassium bromide (KBr)	>99.99%	Desiccator[a], 24 h
NO_2^-	Sodium nitrite (NaNO$_2$)	>99.1%	Desiccator[a], 24 h
NO_3^-	Sodium nitrate (NaNO$_3$)	>100%	120°C, 24 h
PO_4^{3-}	Potassium dihydrogen phosphate (KH$_2$PO$_4$)	>99.8%	120°C, 24h

[a] Vacuum desiccator.

g, NaNO$_3$ 13.7077 g, KH$_2$PO$_4$ 14.3578 g, KBr 14.8940 g, and NaNO$_2$ 14.9980 g were precisely measured and mixed with deionized water to a total weight of 1.000 kg which is referred to as the 10 000 mg kg^{-1} standard solution (10 000 ppm of F^-, Cl^-, NO_2^-, NO_3^-, Br^-, PO_4^{3-}, and SO_4^{2-}, respectively). From the 10 000 ppm standard solution, 50.00 g was taken and diluted with deionized water to a weight of 5.000 kg (100.00 ppm solution). Subsequently, the prepared 100 ppm sample was used in this experiment.

2.3. Resolution between two adjacent peaks

Considering one of the most distinct points of ion chromatography from photometry or atomic absorption spectrometry (AAS), it can simultaneously separate several different ions with only one injection. The extent of separation ability referred to as resolution (R_s) is one of the critical points in ion separation. The corresponding equation is as follows [2,3],

$$R_s = 2(t_1 - t_2)/(W_1 + W_2) \tag{1}$$

where R_s is the resolution value between adjacent peaks. t_1 and t_2 are the retention times of two adjacent eluates, and W_1 and W_2 are the peak widths along the baseline as determined by drawing tangents through the points of inflection in the peaks. To obtain reliable data in the ion chromatogram, a resolution value has to be at least more than 0.5. An R_s value larger than 1.5 is deemed to be sufficient enough for quantitative analysis [3]. Thus, in this

research, we have investigated the achievement of an efficient separation condition ($R_s > 1.50$) with which adjacent peaks of the samples having seven different anions can be completely separated in IC.

3. Results and discussion

3.1. Resolution by the change of eluent composition

For an IC experiment, choosing the proper eluents matched with special characteristics of ion-exchangers in the separator column is one of the most important points. It is known that eluent ions having similar affinity with the analyte ion should be chosen as an eluents [3]. In general, when samples having monovalent and divalent anions are analysed, a mixture of NaHCO$_3$ and Na$_2$CO$_3$ as an eluent is widely used. Especially, in the case of the standard analysis method which is very well known for the separation of seven different anions in aquatic samples, the corresponding mixed eluents are also used [4–6]. In this study, we used an AS4A-SC separation column with which a mixture of 1.8 mM Na$_2$CO$_3$ and 1.7 mM NaHCO$_3$ (eluent A) was used and the flow-rate fixed to 2 ml min^{-1}. The concentration of the seven different samples was 100 mg kg^{-1} each. In previous trials we observed that the use of less than 50 μl of injection volume with respect to the peak size was sufficient for such experiments, and as such, injection volumes below 20 μl were used. The data obtained are shown in Fig. 1A. The figure indicates that F^-, PO_4^{3-}, and SO_4^{2-} ions are well

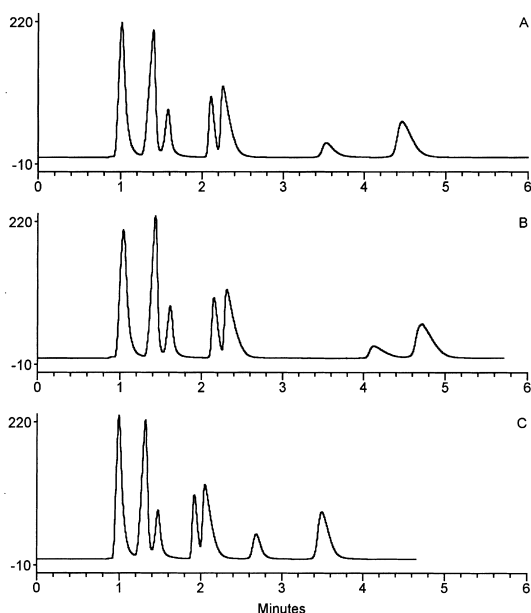Fig. 1. Ion chromatograms for the determination of various inorganic anions. Conditions; flow-rate: 2.0 ml min^{-1}; sample loop: 20 µl; eluent: (A) 1.7 mM NaHCO$_3$+1.8 mM Na$_2$CO$_3$, (B) 2.5 mM NaHCO$_3$+2.0 mM NaOH, (C) 3.0 mM NaHCO$_3$+2.4 mM Na$_2$2CO$_3$.

separated while Cl$^-$, NO$_2^-$, NO$_3^-$, and Br$^-$ ions are not. Generally, controlling the relative retention referred to as selectivity affected by the mobile phase composition is a decisive parameter in resolving adjacent peaks. The eluting power can change their retention times and the selectivity followed by the resolution value shown in Eq. (1). To lengthen the retention time, the elution strength should be decreased. Therefore, in this study, a mixture of 2.5 mM NaHCO$_3$ and 2.0 mM NaOH (eluent B) of which the elution strength is relatively weaker than a mixture of NaHCO$_3$ and Na$_2$CO$_3$ (eluent A) was used. An improvement of the resolution accompanying an increase of the retention time was observed as depicted in Fig. 1B. However, the results were not yet sufficient for good quantitative analysis. Compared with eluent A, the retention times of peaks for PO$_4^{3-}$ and SO$_4^{2-}$ ions having relatively long retention times, were lengthened, accompanying peak broadening while no change for that of monovalent ions was observed. This might be ascribed to the fact that the retention behavior of multivalent ions is dependent on pH change of the eluent [3]. To

shorten the retention time, a mixture of 3.0 mM NaHCO$_3$ and 2.4 mM Na$_2$CO$_3$ (eluent C) which is somewhat more powerful in elution strength was used. The results are shown in Fig. 1C. The retention time for all anions except F$^-$ was shortened. In particular, in the case of PO$_4^{3-}$ and SO$_4^{2-}$ ions, having large affinity to stationary phase, a sharpening of peaks appeared with shortened retention time. Upon only changing the eluent composition, the initial retention time for the latter four ions was so short that the complete separation of all seven ions was not possible.

3.2. Resolution by the change of sample loop

Sample concentration and ion-exchange capacity of the separator column can be decisive factors for determination of injecting sample volume. For seven anions, total ion concentration in 50 µl of 100 ppm is 0.9 µequiv. This concentration does not affect the resolution of each ion because the ion-exchange capacity of the AS4A-SC column used in this study was 20 µequiv. Decrease of injection volume, however, would make the total ion concentration lower, resulting in enhancement of the resolution. To control the injection volume, a sample loop is normally changed. In this experiment, the tube length of the sample loop could be manually made up to 5 µl. A variation of the sample loop was conducted with a fixed flow-rate of 2 ml min^{-1} for all three different eluents. The calculated data from the ion chromatogram are shown in Table 3. The resolution was calculated only for Cl$^-$, NO$_2^-$, Br$^-$, and NO$_3^-$ ions from Eq. (1), indicating that the corresponding resolution slightly increases as volume of sample loop is decreased from 20 µl to 10 µl to 5 µl. However, the resolution is still less than 1.5.

3.3. Resolution by the change of flow-rate

Peak broadening resulting from eddy diffusion, longitudinal diffusion, and the mass transfer effect is one of the serious problems in any chromatographic experiment. These effects are quite dependent on the flow-rate of mobile phase, the stationary phase, diffusion rate, and thickness of stationary phase. Considering van Deemter equation, which relates the column efficiency and the above three effects, the

Table 3
Results obtained from the use of three different eluents in ion chromatography

Eluent	Sample loop (μl)	Resolution	
		Cl^-/NO_2^-	Br^-/NO_3^-
A	20	0.36	0.30
	10	0.42	0.37
	5	0.53	0.44
B	20	0.44	0.30
	10	0.48	0.43
	5	0.61	0.44
C	20	0.32	0.23
	10	0.42	0.37
	5	0.46	0.38

A: 1.7 mM NaHCO$_3$+1.8 mM Na$_2$CO$_3$.
B: 2.5 mM NaHCO$_3$+2.0 mM NaOH.
C: 3.0 mM NaHCO$_3$+2.4 mM Na$_2$2CO$_3$.

theoretical plate number is proportional to the flow-rate of eluent. Decrease of flow-rate gives a decrease of mass transfer effect. So, a lower theoretical plate height brings improvement of column efficiency. Table 4 represents resolution values obtained from ion pairs of Cl^-/NO_2^- and Br^-/NO_3^- using 20, 10, and 5 μl sample loops and flow-rates varied from 1.1 to 0.8 to 0.5 ml min^{-1}, respectively. In the case of 1.1 ml min^{-1} of flow-rate, no big changes in resolution values were observed for each ion pair. The use of eluent B, having somewhat weaker elution

power, gave better resolution values. However, the resolution value did not reach 1.5 at which most peaks can be sufficiently separated. In all case of A–C, when the flow-rate was 0.8 ml min^{-1}, the resolution value was improved to be over 0.9, except using a 20 μl sample loop. Interestingly, in the case of ion pair Cl^-/NO_2^-, the use of 5 μl of sample loop with 0.5 ml min^{-1} of flow-rate provided 1.96, 1.96, and 1.85, excellent resolution values, for eluents A, B, and C, respectively. Also, for Br^-/NO_3^-, remarkable resolution values were obtained using the same separation conditions. So, where the flow-rate of eluent of 0.5 ml min^{-1} and a 5 μl sample loop were applied, a highly concentrated sample solution such as 100 mg kg^{-1} of several anions could be directly separated without making any diluted solution. Fig. 2 indicates the influence of eluent change on ion chromatogram. In the case of a mixture of 1.8 mM Na$_2$CO$_3$ and 1.7 mM NaHCO$_3$ as well as a mixture of 2.5 mM NaHCO$_3$ and 2.0 mM NaOH as eluents, the ion peaks for PO_4^{3-} and SO_4^{2-} were observed to be broad, at around 20 min of total separation time. Using 2.4 mM Na$_2$CO$_3$ and 3.0 mM NaHCO$_3$ as eluents provided a shorter retention time less than 15 min with excellent separation efficiency.

In conclusion, we have found improved separation conditions with which 100 ppm of seven anions existing in aqueous solution can be efficiently separated without any further dilution. For the resolution

Table 4
Results obtained from the use of three different eluents in ion chromatography

Eluent	Flow-rate (ml min^{-1})	Resolution					
		20[a]		10[a]		5[a]	
		Cl^-/NO_2^-	Br^-/NO_3^-	Cl^-/NO_2^-	Br^-/NO_3^-	Cl^-/NO_2^-	Br^-/NO_3^-
A	1.1	0.63	0.48	0.83	0.70	0.89	0.84
	0.8	0.86	0.65	1.10	0.97	1.29	1.16
	0.5	1.34	0.87	1.80	1.51	1.96	1.84
B	1.1	0.88	0.67	0.99	0.98	1.20	1.12
	0.8	1.14	0.93	1.31	1.18	1.36	1.23
	0.5	1.43	1.05	1.77	1.50	1.96	1.85
C	1.1	0.59	0.37	0.75	0.61	0.85	0.69
	0.8	0.89	0.65	1.13	0.92	1.24	1.07
	0.5	1.29	0.96	1.53	1.35	1.85	1.67

[a] Sample loop size (μl).
A: 1.7 mM NaHCO$_3$+1.8 mM Na$_2$CO$_3$.
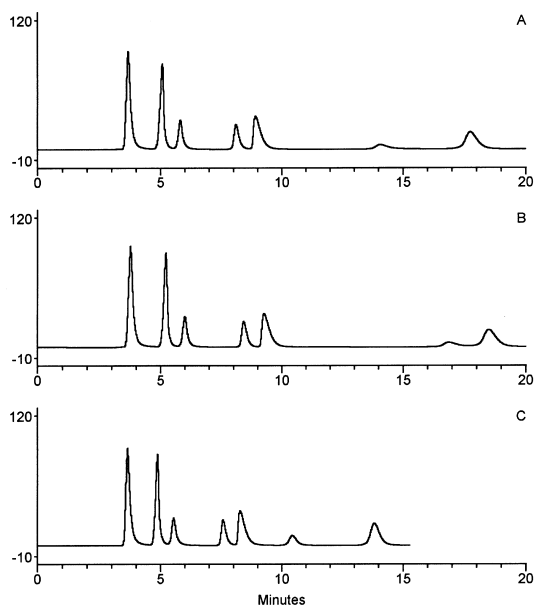B: 2.5 mM NaHCO$_3$+2.0 mM NaOH.
C: 3.0 mM NaHCO$_3$+2.4 mM Na$_2$2CO$_3$.

Fig. 2. Ion chromatograms for the determination of various inorganic anions. Conditions; flow-rate: 0.5 ml min^{-1}; sample loop: 5 μl; eluent: (A) 1.7 mM NaHCO$_3$ + 1.8 mM Na$_2$CO$_3$, (B) 2.5 mM NaHCO$_3$ + 2.0 mM NaOH, (C) 3.0 mM NaHCO$_3$ + 2.4 mM Na$_2$CO$_3$.

of ion pair of Cl$^-$/NO$_2^-$ and Br$^-$/NO$_3^-$, a number of investigations including changing sample loop, com-

position of eluents, and flow-rates were attempted. Using a solution of 2.0 mM Na$_2$CO$_3$ and 2.5 mM NaHCO$_3$ as eluents, 0.5 ml min^{-1} of flow-rate, and a 5 μl sample loop gave an excellent resolution value larger than 1.6. In this condition, all seven ions can be eluted in less than 15 min of analysis time.

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