Short communication

Simultaneous determination of six cations in mineral water by single-column ion chromatography[1]

Jong-Hun Kim[a],*, Joung-Hae Lee[b]

[a]*Department of Chemistry, Jeonju University, Jeonju 560-759, South Korea*
[b]*Korea Research Institute of Standards and Science, Taejeon 305-600, South Korea*

Abstract

The analytical conditions for the simultaneous determination of Li^+, Na^+, K^+, NH_4^+, Mg^{2+} and Ca^{2+} by ion chromatography using a Waters IC-PAK CM/D column were optimised with respect to flow-rate and eluents. Optimum separation of the cations was achieved using 5 mM HNO_3+0.1 mM EDTA with a flow-rate of 0.6 ml/min and an analytical run time of 8 min. The results of the analysis of cations in seventeen commercially available South Korean bottled waters are presented. Although there is a reference value for drinking water quality in South Korea of 0.5 ppm, the concentration of NH_4^+ in the water analysed was in the range 0.3–3.0 ppm. © 1997 Elsevier Science B.V.

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1. Introduction

The development of ion chromatographic columns containing poly(butadiene–maleic acid)-coated silica in 1989 [1] has enabled the analysis of a wide range of inorganic anions and cations in a variety of different matrices [2–5].

Although there is a plethora of reports particularly relating to the separation of anions in water [6,7], few are concerned with the simultaneous analysis of alkali metals, alkali-earth metals and the ammonium ion in water samples by non-suppressed ion chromatography.

This study reports the development of a method

for the separation of Li^+, Na^+, K^+, NH_4^+, Mg^{2+} and Ca^{2+} using a Waters IC-PAK CM/D column and eluents containing 3 mM HNO_3+0.1 mM EDTA and 5 mM HNO_3+0.1 mM EDTA. The method was applied to the analysis of seventeen commercially available South Korean mineral waters.

2. Experimental

The ion chromatographic system consisted of a SLC 100 pump (Samsung, Seoul, South Korea), a Rheodyne 9125 injection valve with a 20 μl sample loop, a conductivity detector, Model SLC 320 (Samsung), and a D520 integration system (Youngin, Seoul, South Korea). The Waters IC-PAK CM/D cation column (200×4.6 mm I.D.) contained poly-

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*Corresponding author.
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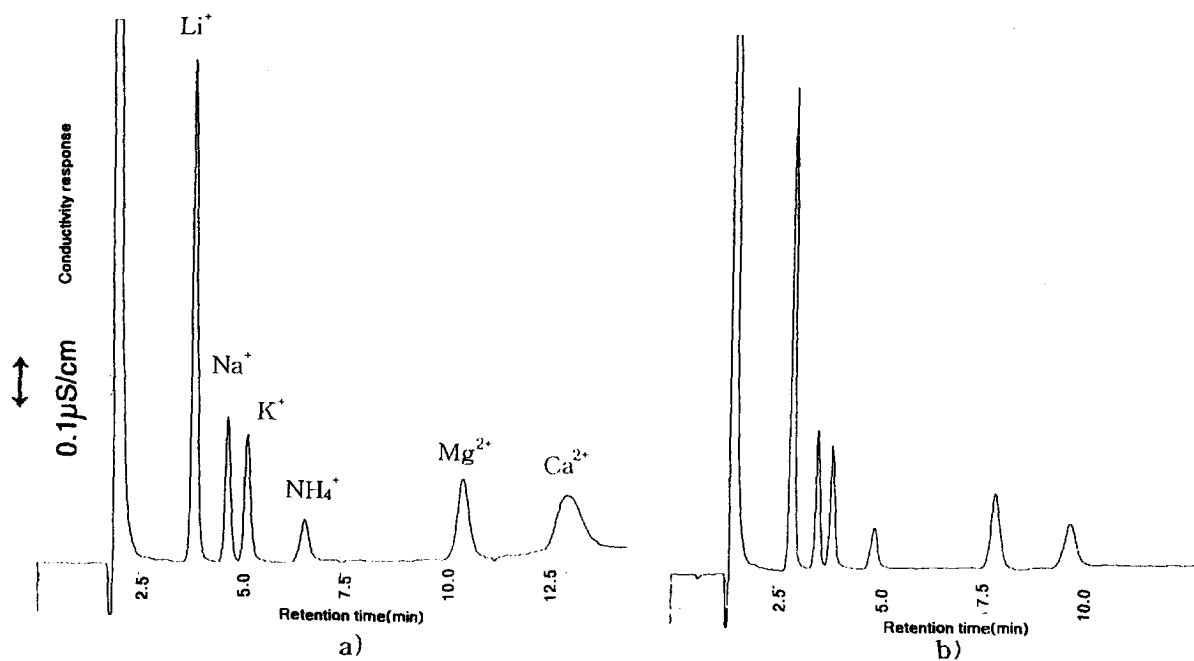
Fig. 1. Effect of flow-rate on the separation of Li^+, Na^+, K^+, NH_4^+, Mg^{2+} and Ca^{2+} ions. Column: Waters IC-PAK CM/D; eluent: 3 mM HNO_3; sample condition: 3 ppm; injection volume: 20 µl; flow-rate: (a) 0.6 ml/min (b) 0.8 ml/min.

Fig. 2. Effect of flow-rate on the separation of Li^+, Na^+, K^+, NH_4^+, Mg^{2+} and Ca^{2+} ions. Column: Waters IC-PAK CM/D; eluent: 5 mM HNO_3; sample condition: 3 ppm; injection volume: 20 µl; flow-rate: (a) 0.6 ml/min (b) 0.8 ml/min.
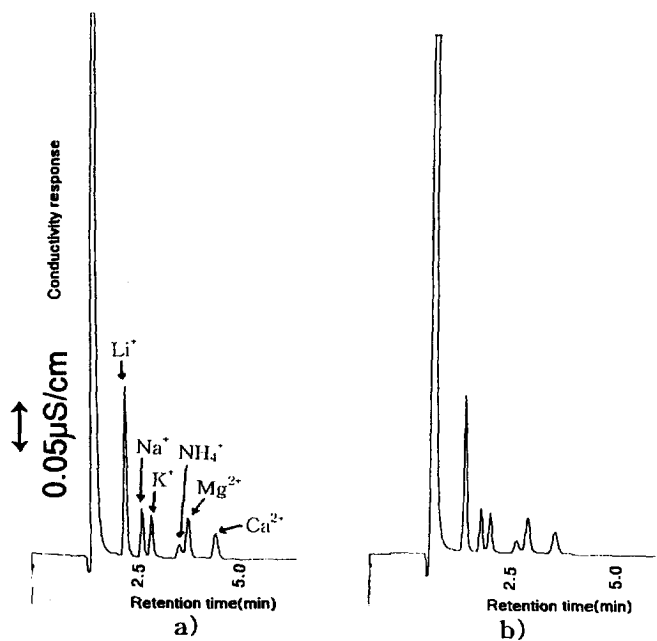
(butadiene–maleic acid) coated onto amorphous silica.

All chemicals were purchased from Junsei (Tokyo, Japan) or Aldrich (Seoul, South Korea). Deionized water purified by additional ion-exchange and filtration through activated charcoal and a 0.4 μm filter (Millipore, Milli-Q) was used for the preparation of standards and eluents.

Eluents were prepared with freshly deionized water and degassed for about 15 min in an ultrasonic bath. Standard solutions were prepared containing each cation at a concentration of 3 ppm.

3. Results and discussion

The mobile phase used in single-column ion chromatography (SCIC) must have a strong affinity for the ion-exchange resin so that effective separation of the analyte ions is achieved. In the development of the method described in this paper, HNO_3 at various concentrations, containing EDTA was used to effect the simultaneous analysis of Li^+, Na^+, K^+, NH_4^+, Mg^{2+} and Ca^{2+} in water samples.

3.1. Effect of flow-rate of eluent and concentration of HNO_3

Analysis of standard solutions using 3 mM and 5 mM HNO_3 as eluents and flow-rates of 0.6 ml/min and 0.8 ml/min indicated that the most efficient separation of the cations was obtained with an eluent strength of 3 mM HNO_3 and a flow-rate of 0.6 ml/min (Figs. 1 and 2). Although good separation was obtained with a flow-rate of 0.8 ml/min, there was a disadvantage to using this flow-rate in that the pump pressure was relatively high at about 1200 p.s.i. (1 p.s.i.=6894.76 Pa). Retention times of the cations were reduced significantly when a flow-rate of 0.8 ml/min as compared to 0.6 ml/min was used. Retention times were reduced further using 5 mM HNO_3 as eluent but incomplete separation of NH_4^+ and Mg^{2+} was obtained.

3.2. Effect of HNO_3 containing EDTA as eluent

EDTA competes more strongly with solute ions of doubly charged ions than HNO_3 and the inclusion of EDTA yields increased resolution and peak symmetry.
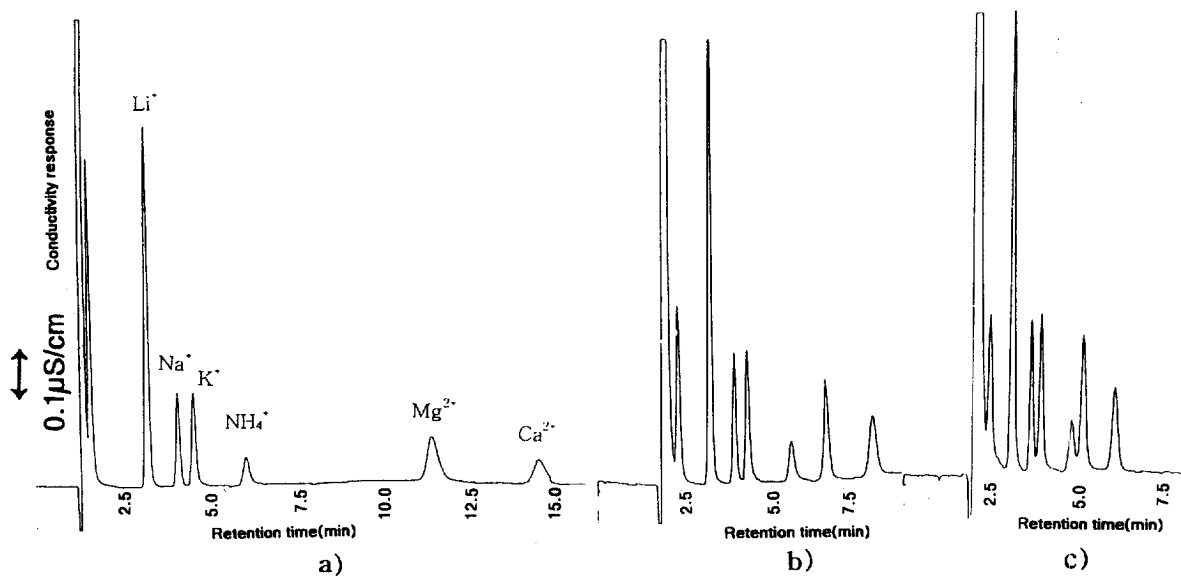

Fig. 3. Effect of flow-rate on the separation of Li^+, Na^+, K^+, NH_4^+, Mg^{2+} and Ca^{2+} ions. Column: Waters IC-PAK CM/D; sample concentration: 3 ppm; injection volume: 20 μl; flow-rate: (a) 0.8 ml/min (b) and (c) 0.6 ml/min. Eluent: (a) 3 mM HNO_3+0.1 mM EDTA (H_4Y), (b) 5 mM HNO_3+0.1 mM EDTA (H_4Y), (c) 5 mM HNO_3+0.1 mM EDTA (Na_2H_2Y).

When 0.1 mM EDTA either in the free (H$_4$Y) or sodium (Na$_2$H$_2$Y) forms was added to 5 mM HNO$_3$ (Fig. 3b,c) the resolution of Na$^+$ and K$^+$ was less than that obtained when the eluent contained 3 mM HNO$_3$ and 0.1 mM EDTA (H$_4$Y) (Fig. 3a). The latter eluent at a flow-rate of 0.8 ml/min yielded complete separation of the cations but with longer retention times. Increasing the concentration of EDTA from 0.1 mM to 0.2 mM did not result in an increase in the retention time of the cations provided that the HNO$_3$ concentration was kept constant.

3.3. Peak area variations with flow-rate

The effect of flow-rate of the eluent on the peak areas of the cations was examined (Fig. 4). For each of the eluents, the peak areas of the cations decreased with increasing flow-rate. The greatest effect was evident for Li$^+$ regardless whether the eluent comprised 3 mM HNO$_3$ and 0.1 mM or 0.2 mM EDTA or 5 mM HNO$_3$ and 0.1 mM EDTA. For all elements, the maximum peak area was obtained when a flow-rate of 0.6 ml/min was used.

3.4. Calibration curves

A linear relationship between peak areas and ion concentration was found experimentally for all the six cations under investigation (Fig. 5 and Table 1).

Table 1
Linear regression analysis and simple correlation coefficient of the six cation calibration plots

Ion	Regression equation[a]	Correlation coefficient (r)
Li$^+$	$y_1 = 57\ 241.1x + 7276.3$	$r_1 = 0.9969$
	$y_2 = 78\ 202.6x + 15\ 093.4$	$r_2 = 0.9991$
Na$^+$	$y_1 = 15\ 530.2x + 4394.8$	$r_1 = 0.9976$
	$y_2 = 20\ 573.6x + 6393.0$	$r_2 = 0.9990$
K$^+$	$y_1 = 18\ 741.8x + 2212.6$	$r_1 = 0.9972$
	$y_2 = 24\ 438.6x + 2985.6$	$r_2 = 0.9991$
NH$_4^+$	$y_1 = 8457.4x + 3371.8$	$r_1 = 0.9908$
	$y_2 = 11\ 375.0x + 3657.6$	$r_2 = 0.9987$
Mg^{2+}	$y_1 = 22\ 532.9x + 8360.1$	$r_1 = 0.9972$
	$y_2 = 31\ 090.6x + 4508.4$	$r_2 = 0.9998$
Ca^{2+}	$y_1 = 16\ 222.4x + 6437.9$	$r_1 = 0.9901$
	$y_2 = 22\ 638.5x + 4262.4$	$r_2 = 0.9998$

[a] y_1 represents the peak area and x represents the concentration of cations and r_1 is the correlation coefficient using an eluent of 3 mM HNO$_3$ + 0.1 mM EDTA and a flow-rate of 0.8 ml/min.
y_2 represents the same as y_1, and r_2 is the correlation coefficient using an eluent of 5 mM HNO$_3$ + 0.1 mM EDTA and a flow-rate of 0.6 ml/min.

Linear regression analysis showed that there was close correlation between the results obtained by SCIC employing two eluents, namely 3 mM HNO$_3$ + 0.1 mM EDTA and 5 mM HNO$_3$ + 0.1 mM EDTA.
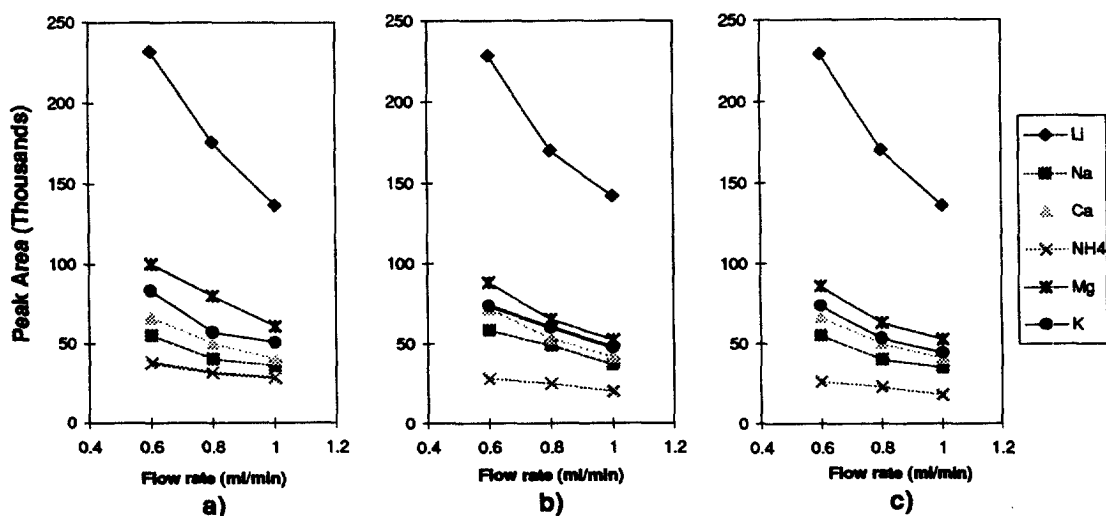

Fig. 4. Effect of eluent composition and flow-rate on peak area of cations in a standard solution containing 3 ppm of each cation. (a) 3 mM HNO$_3$ + 0.1 mM EDTA, (b) 3 mM HNO$_3$ + 0.2 mM EDTA, (c) 5 mM HNO$_3$ + 0.1 mM EDTA.
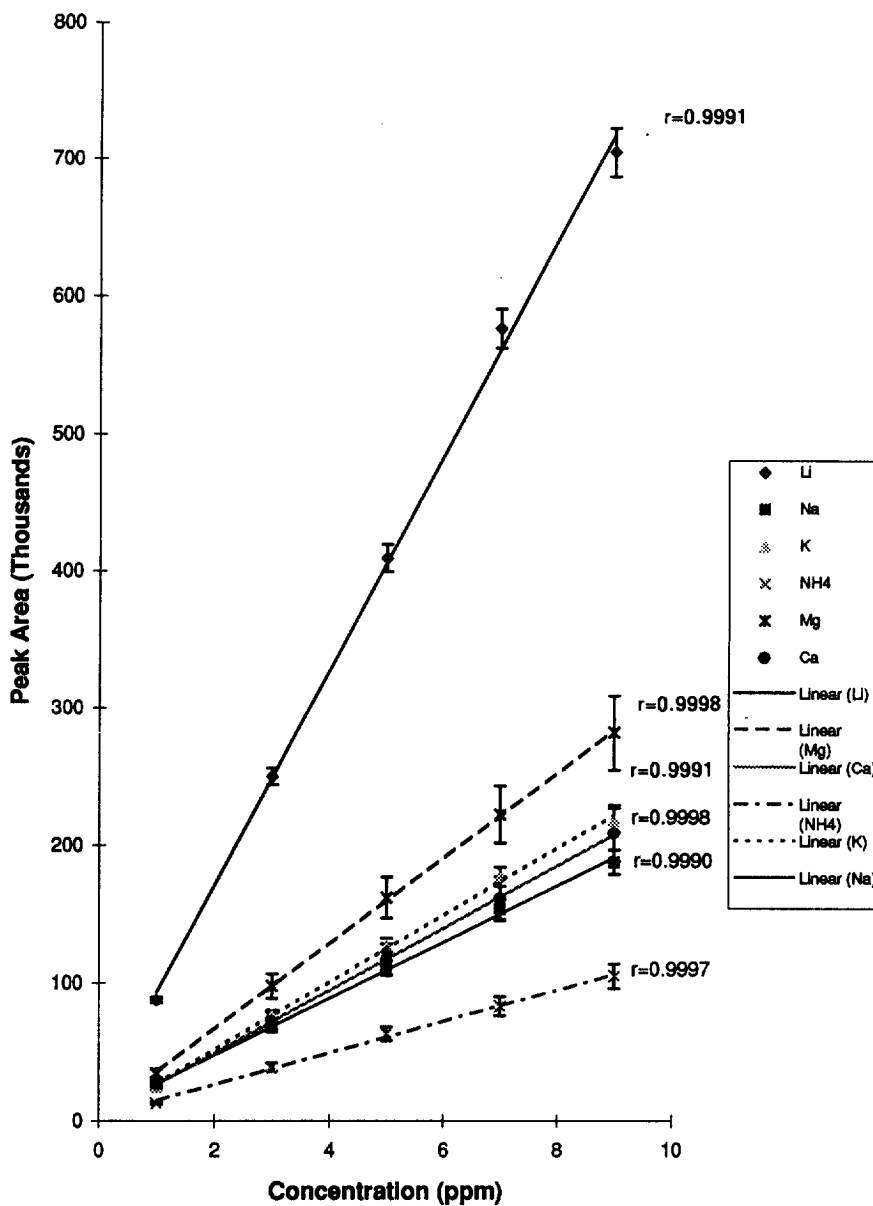
Fig. 5. Calibration curve of standard solutions containing Li$^+$, Na$^+$, K$^+$, NH$_4^+$, Mg^{2+} and Ca^{2+} ions. Eluent: 5 mM HNO$_3$+0.1 mM EDTA. Flow-rate: 0.6 ml/min.

The correlation coefficient (r) varied between 0.9901 and 0.9998 for the respective methods. However, it should be noted that the correlation coefficient r_2 was always higher than r_1 (Table 1) and can be explained by the fact that the increased HNO$_3$ concentration reduces the elution times of the ions

and hence the peak areas (Fig. 4). The method was validated using reference water containing a known concentration of each of the six cations was obtained from the Korea Research Institute of Standards and Science and the results expressed in Table 2 have a 95% confidence level.

Table 2
Analysis data for cation concentration in South Korean bottled mineral waters

Sample	Eluent	Li$^+$	Na$^+$ [a]	K$^+$	NH$_4^+$	Mg^{2+}	Ca^{2+} [a]
W-1	(a)	ND	9.1	ND	0.8	1.3	27.9
	(b)	ND	9.5	ND	0.5	1.5	30.1
W-2	(a)	ND	21.3	ND	3.0	6.1	15.3
	(b)	ND	21.5	ND	3.0	6.6	17.2
W-3	(a)	ND	12.5	ND	1.2	6.1	31.4
	(b)	ND	12.9	ND	1.6	5.7	31.5
W-4	(a)	0.04	15.0	ND	0.5	8.0	22.9
	(b)	0.04	14.6	ND	0.6	8.2	23.6
W-5	(a)	ND	3.3	ND	1.0	2.9	25.1
	(b)	ND	3.3	ND	1.0	2.9	25.7
W-6	(a)	ND	3.3	ND	ND	0.2	9.2
	(b)	ND	3.3	ND	0.3	0.2	10.7
W-7	(a)	ND	14.5	ND	0.6	11.1	12.7
	(b)	ND	14.3	ND	0.7	11.6	25.6
W-8	(a)	ND	6.9	ND	0.8	5.3	22.4
	(b)	ND	6.9	ND	0.9	5.5	24.4
W-9	(a)	0.05	34.8	ND	2.3	17.9	50.1
	(b)	0.05	33.0	ND	2.5	18.7	52.6
W-10	(a)	0.02	63.3	ND	0.6	2.0	9.2
	(b)	ND	68.8	ND	0.5	1.9	9.0
W-11	(a)	ND	1.4	ND	0.3	5.6	12.2
	(b)	ND	1.5	ND	0.5	6.1	13.3
W-12	(a)	ND	23.3	ND	1.2	8.3	33.2
	(b)	ND	25.1	ND	1.4	9.1	36.1
W-13	(a)	ND	8.6	ND	1.6	5.2	11.1
	(b)	ND	9.6	ND	1.6	6.6	12.8
W-14	(a)	ND	6.5	ND	0.3	0.7	7.2
	(b)	ND	6.8	ND	0.3	0.6	8.4
W-15	(a)	ND	3.3	ND	1.0	4.1	31.9
	(b)	ND	4.0	ND	1.4	5.0	38.2
W-16	(a)	ND	11.2	ND	1.2	4.7	38.7
	(b)	ND	11.8	ND	1.5	1.0	20.9
W-17	(a)	0.02	8.0	ND	0.6	5.7	4.3
	(b)	ND	7.9	ND	0.7	5.7	7.1

Values as ppm. ND: not detected. (a) Analysis carried out using an eluent of 5 mM HNO$_3$+0.1 mM EDTA and a flow-rate of 0.6 ml/min. (b) Analysis carried out using an eluent of 3 mM HNO$_3$+0.1 mM EDTA and a flow-rate of 0.8 ml/min. [a] Values are indicative only.

3.5. Application of the method to the analysis of commercially available bottled waters

Prior to analyses, the water samples were filtered through a 0.45 μm membrane filter. The method enabled the analyses of commercially available South Korean mineral waters which contained the cations Li^+, Na^+, K^+, NH_4^+, Mg^{2+} and Ca^{2+} at concentrations of less than 9 ppm. The results are given in Table 2. It should be noted that the concentrations of Na^+ and Ca^{2+} greater than 9 ppm were obtained by extrapolation and should be regarded as indicative. The concentrations of K^+ and, in most cases, Li^+ in the waters were below the limit of detection of the present method although the use of a larger loop volume would probably allow the determination of these two elements. The limit of detection for each cation was determined from the regression equations and based on a signal-to-noise ratio of 3:1. The limits of detection for Li^+ and K^+ were determined to be 0.01 and 0.05 ppm, respectively. The detection limits for Na^+, NH_4^+, Mg^{2+} and Ca^{2+} were 0.05, 0.1, 0.08 and 0.08 ppm, respectively.

In South Korea, the maximum recommended value for NH_4^+ in drinking water is 0.5 ppm. In only two of the water samples examined was the concentration of NH_4^+ equal to or less than the value. In one sample (W-2), the recommended value was exceeded by a factor of 6.

Two eluent systems were used, namely 3 mM $HNO_3 + 0.1$ mM EDTA at a flow-rate of 0.8 ml/min and 5 mM $HNO_3 + 0.1$ mM EDTA at a flow-rate of 0.6 ml/min. The former yielded baseline separation of Na^+ and K^+ in standard solutions and the analysis time was greater than that using the latter solvent. However, it is evident from Table 2 that the values obtained for the cations are similar irrespective of which eluent system is used to effect the analysis.

Acknowledgments

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