Characteristics of New Ion Chromatography Columns for High Throughput Ion Analysis

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Introduction

- Ion chromatography (IC) is a versatile and widely accepted technique for the analysis of inorganic and organic ions. It is characterized as a highly selective and sensitive analytical method.

- In many cases IC has superseded conventional wet chemistry methods such as titration, photometry, gravimetry, and colorimetry.

- The current trend in HPLC is high throughput analysis using ultra high pressure systems and shorter columns with smaller particles.

- To introduce this trend to IC, we have developed novel analytical columns with small particles for ion analysis.

- We evaluated the fundamental characteristics of these new TSK-GEL SuperIC-HS columns and the results are reported here. We investigated the effect of flow rate on column efficiency, selectivity as a function of column temperature, and resistance to organic solvents in addition to other characteristics.

- Furthermore, quantitative performance of ion analysis was evaluated using the ion chromatograph IC-2010 (Tosoh). Finally, we confirmed the excellent performance showing the high throughput analysis of several important environmental samples

Experimental

Columns – Tosoh Corporation (Japan)

- TSKgel SuperIC-Anion HS, 4.6mm ID x 10cm
- TSKguardcolumn SuperIC-Anion HS, 4.6mm ID x 1cm
- TSKgel SuperIC-Cation HS, 4.6mm ID x 10cm
- TSKguardcolumn SuperIC-Cation HS, 4.6mm ID x 1cm

Instrumentation

Instrument: Ion Chromatograph IC-2010 (Tosoh)
Data processing: IC-2010 WorkStation (Tosoh)

Chemicals and Reagents

All ions and reagents were purchased from Wako Chemicals (Osaka).

Water for eluent and sample preparation was purified with a Milli-Q® water purification system.

Environmental samples were taken in our office and a neighborhood river.
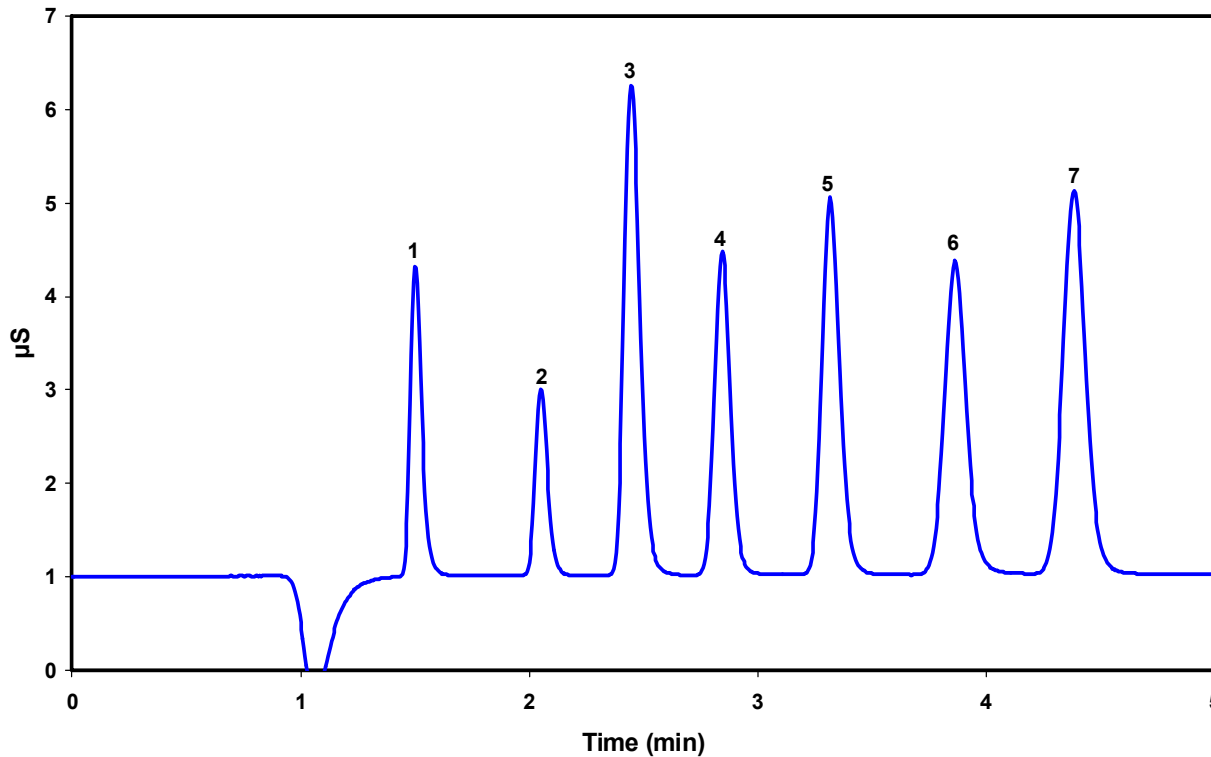
Separation of common ions on TSK-GEL SuperIC HS columns

Table 1: Specifications of TSK-GEL SuperIC HS columns

	TSKgel SuperIC-Anion HS	TSKgel SuperIC-Cation HS
Part No.	0022766	0022768
Column size	4.6mm ID x 10cm	4.6mm ID x 10cm
Container material	PEEK	PEEK
Gel material	Hydrophilic polymer	Poly(styrene-divinylbenzene)
Particle size	3.5µm	3.0µm
Functional group	Quaternary ammonium	Carboxylic acid
Capacity	ca. 30meq/L-gel	ca. 1.0eq/L-gel
Theoretical Plates (TP)	$\geq 8{,}000$ (SO_4^{2-})	$\geq 4{,}500$ (Na^+)

Separation of common ions on TSK-GEL SuperIC HS columns

Figure 1: Separation of 7 common anions

Columns: TSKgel SuperIC-Anion HS, 4.6mm ID x 10cm
 TSKguardcolumn SuperIC-A HS, 4.6mm ID x 1cm
Mobile phase: 3.8mmol/L $NaHCO_3$ + 3.0mmol/L Na_2CO_3
Flow rate: 1.5mL/min
Detection: Suppressed conductivity
Temperature: 40°C
Injection vol.: 30μL
Pressure: 16MPa
Suppressor gel: TSKsuppress IC-A
Samples: 1. fluoride (1mg/L) 2. chloride (1mg/L)
3. nitrite (5mg/L) 4. bromide (5mg/L)
5. nitrate (5mg/L) 6. phosphate (10mg/l)
7. sulfate (5mg/L)

Separation of common ions on TSK-GEL SuperIC HS columns

## Figure 2: Separation of 6 common cations
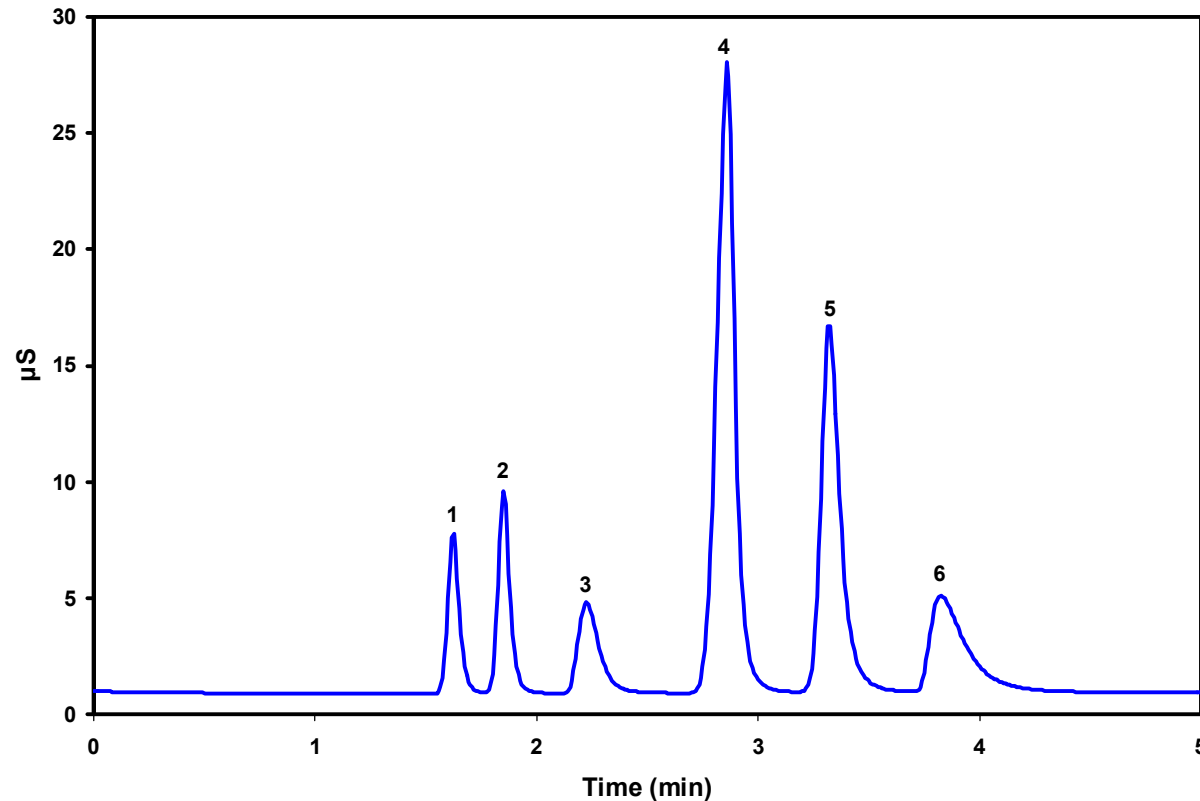
Columns: TSKgel SuperIC-Cation HS, 4.6mm ID x 10cm
TSKguardcolumn SuperIC-C HS, 4.6mm ID x 1cm
Mobile phase: 3.0mmol/L Methanesulfonic acid
+ 0.4mmol/L 18-crown 6-ether + 0.2mmol/L L-Histidine
Flow rate: 1.2mL/min
Detection: Suppressed conductivity
Temperature: 40°C
Injection vol.: 30μL
Pressure: 16MPa
Suppressor gel: TSKsuppress IC-C
Samples: 1. lithium (0.5mg/L) 2. sodium (2 mg/L)
3. ammonium (2 mg/L) 4. magnesium (5 mg/L)
5. calcium (5 mg/L) 6. potassium (5 mg/L)

Evaluation of quantitative performance

Figure 3: Calibration curve of each ion
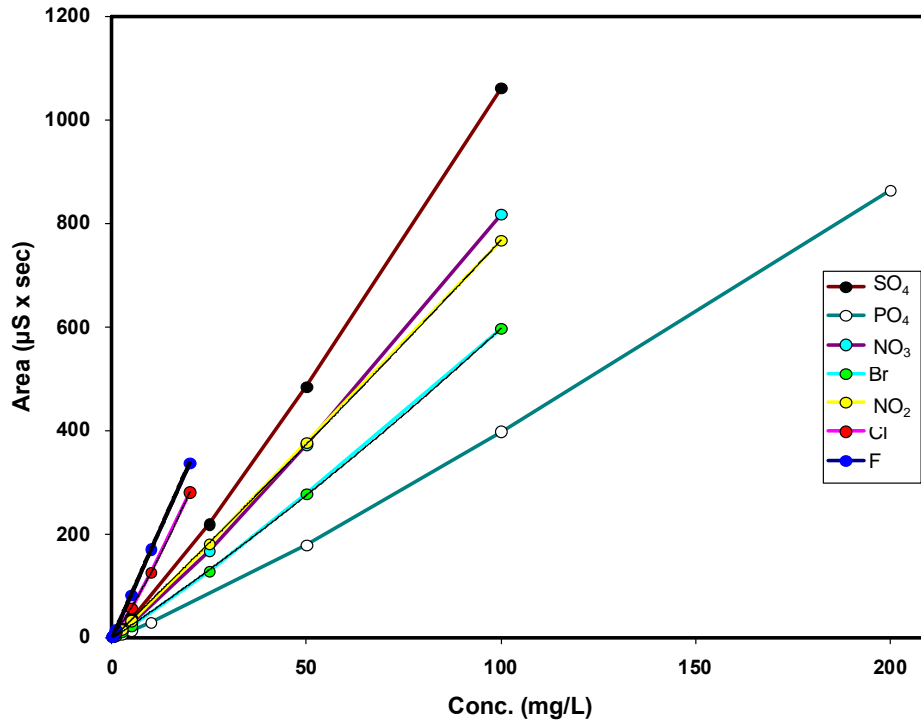
Approximation: Quadratic on each anion
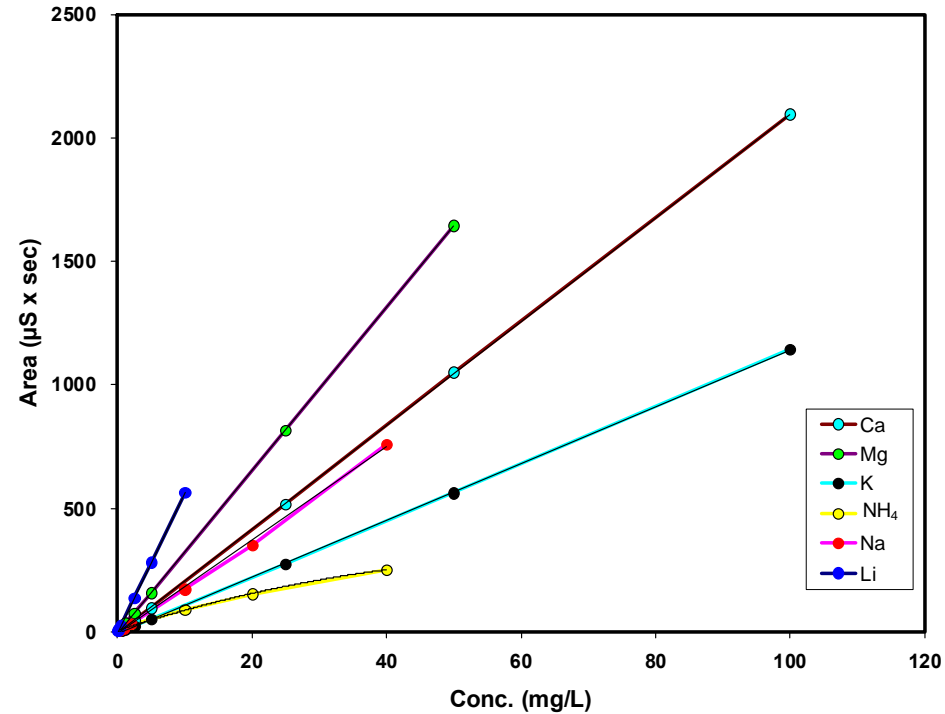
Approximation: NH$_4$$^+$ - quadratic
Other cations - linear

Evaluation of quantitative performance

Table 2: Limits of detection of ions

Anions	F^-	Cl^-	NO_2^-	Br^-	NO_3^-	PO_4^{3-}	SO_4^{2-}
(µg/L)	0.9	1.3	3.0	3.9	3.6	8.2	3.6
Cations	Li^+	Na^+	NH_4^+	K^+	Mg^{2+}	Ca^{2+}	
(µg/L)	0.1	0.3	0.3	3.0	0.2	0.4	

Analysis conditions were the same as in figures 1 and 2.

LODs were calculated by S/N = 3

Basic characteristics of TSK-GEL SuperIC HS columns

Figure 4: Ion retention as a function of column temperature
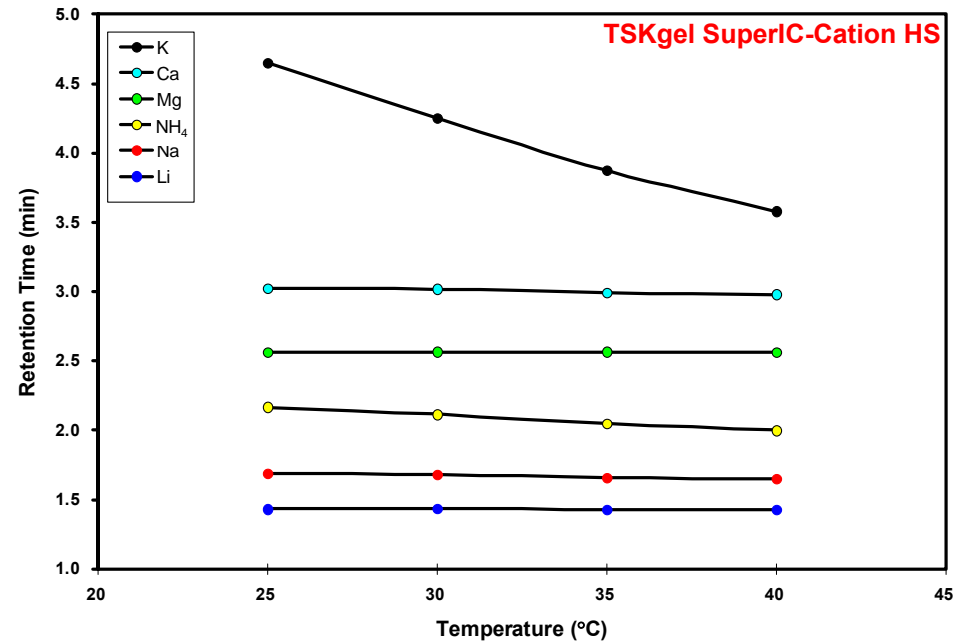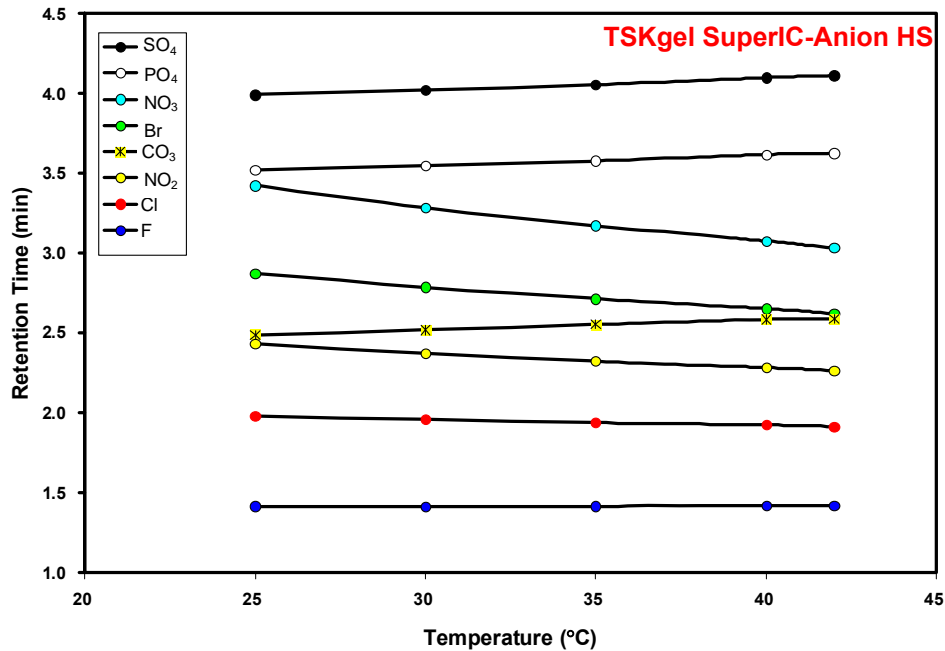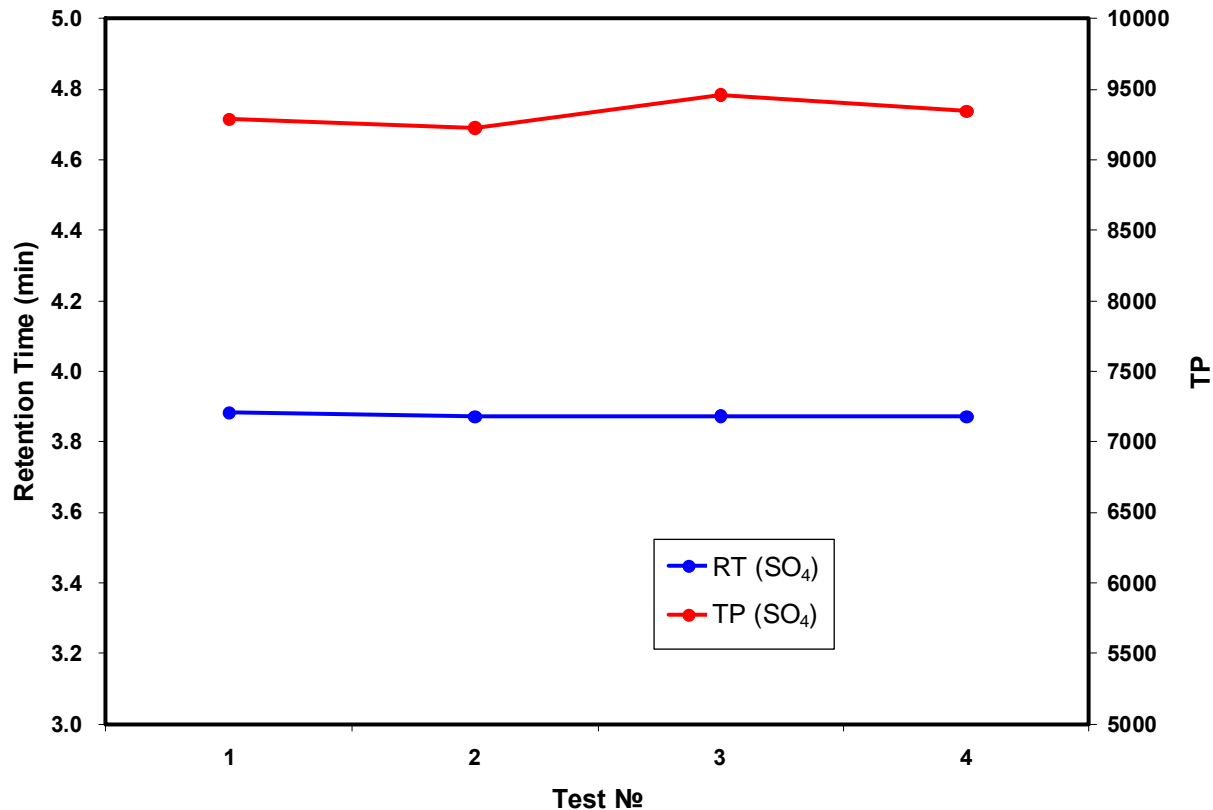
Basic characteristics of TSK-GEL SuperIC HS columns
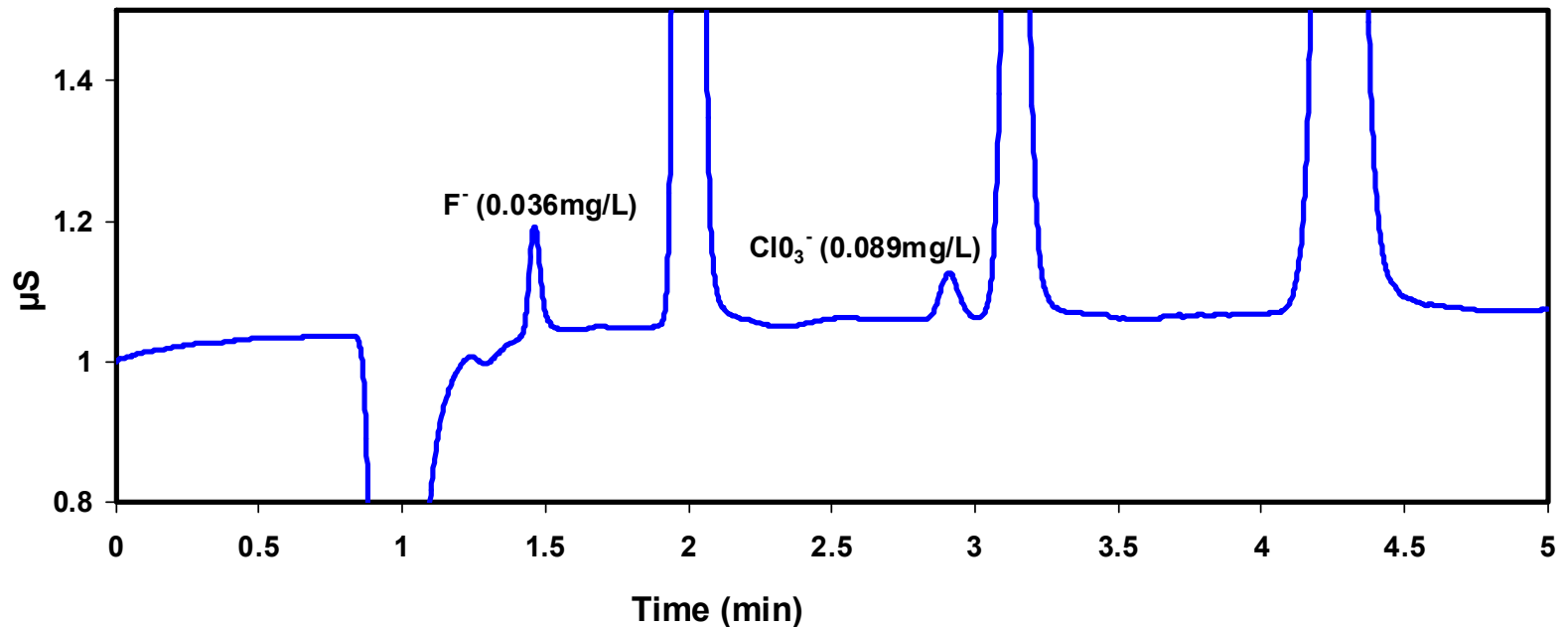
Figure 5: Van Deemter curves
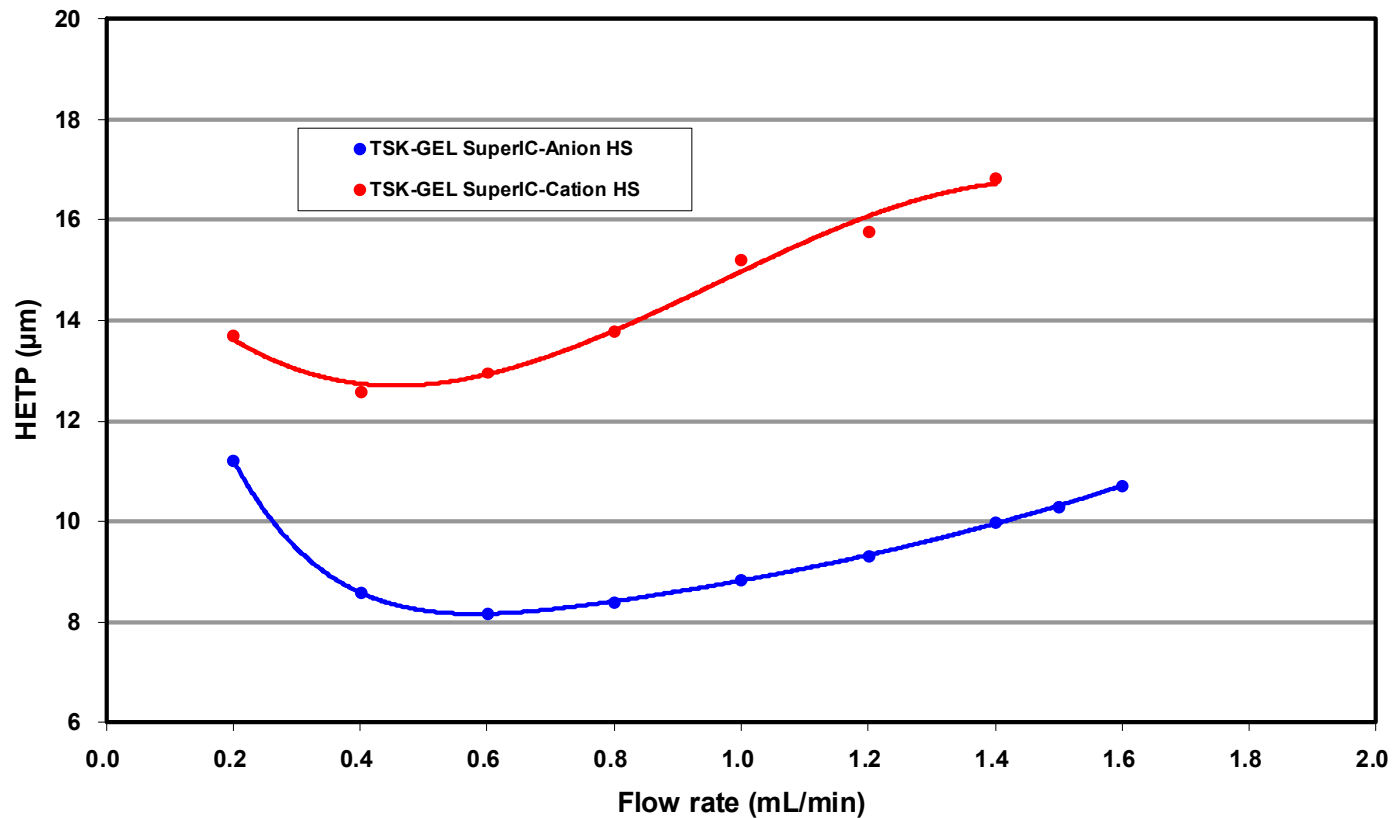
Figure 6: Effect of organic solvents on retention and efficiency of TSKgel SuperIC-Anion HS column

Application to environmental samples

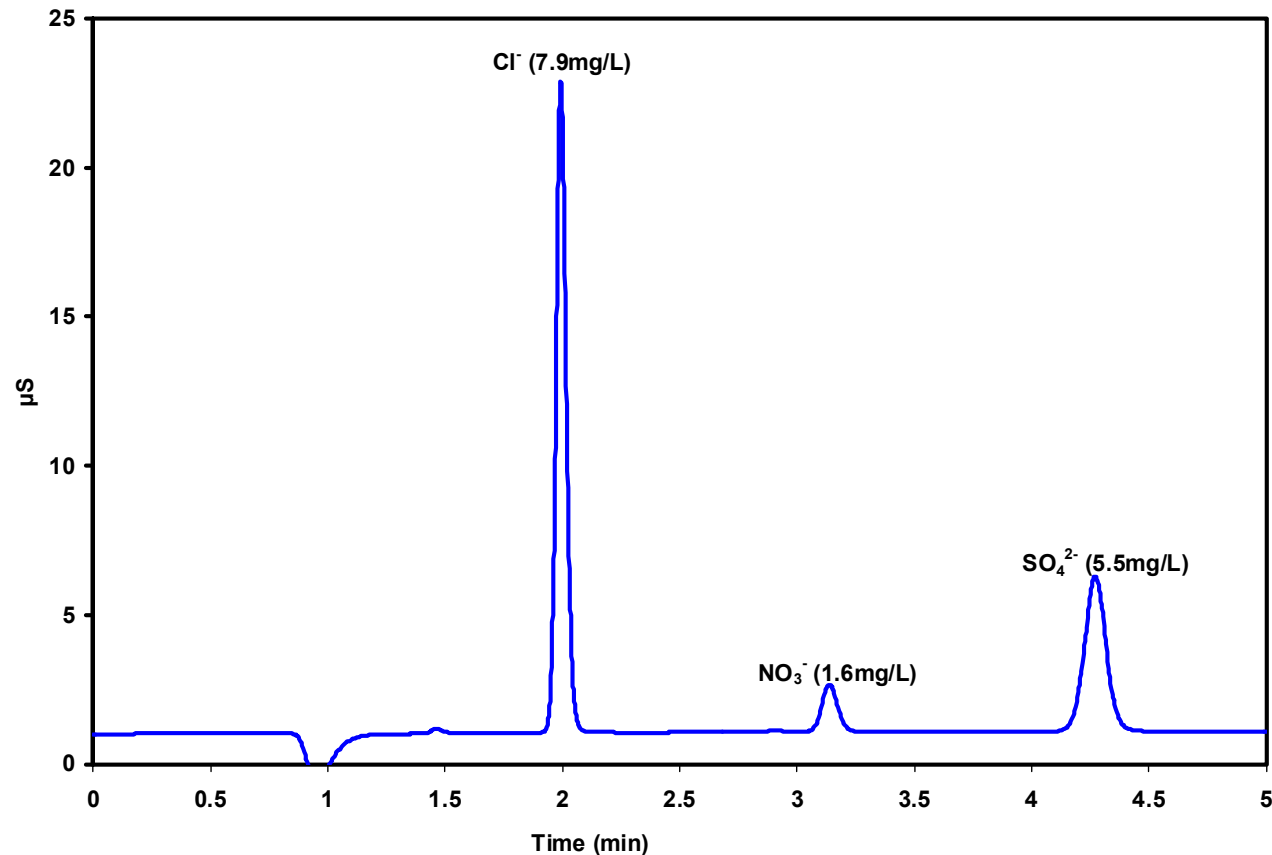## Figure 7: Analysis of environmental samples – Tap Water

F⁻ (0.036mg/L)

ClO₃⁻ (0.089mg/L)

Analysis conditions were the same as in figure 1.

Application to environmental samples

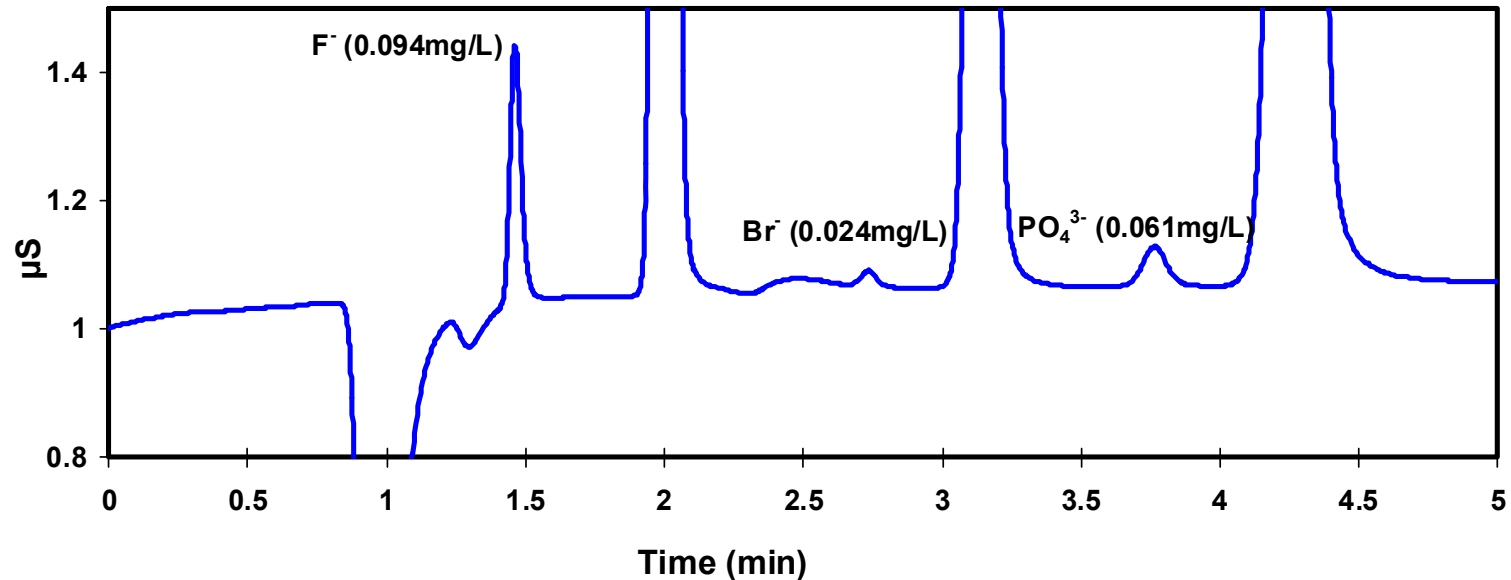## Figure 7: Analysis of environmental samples – Tap Water, cont.

Analysis conditions were the same as in figure 1.

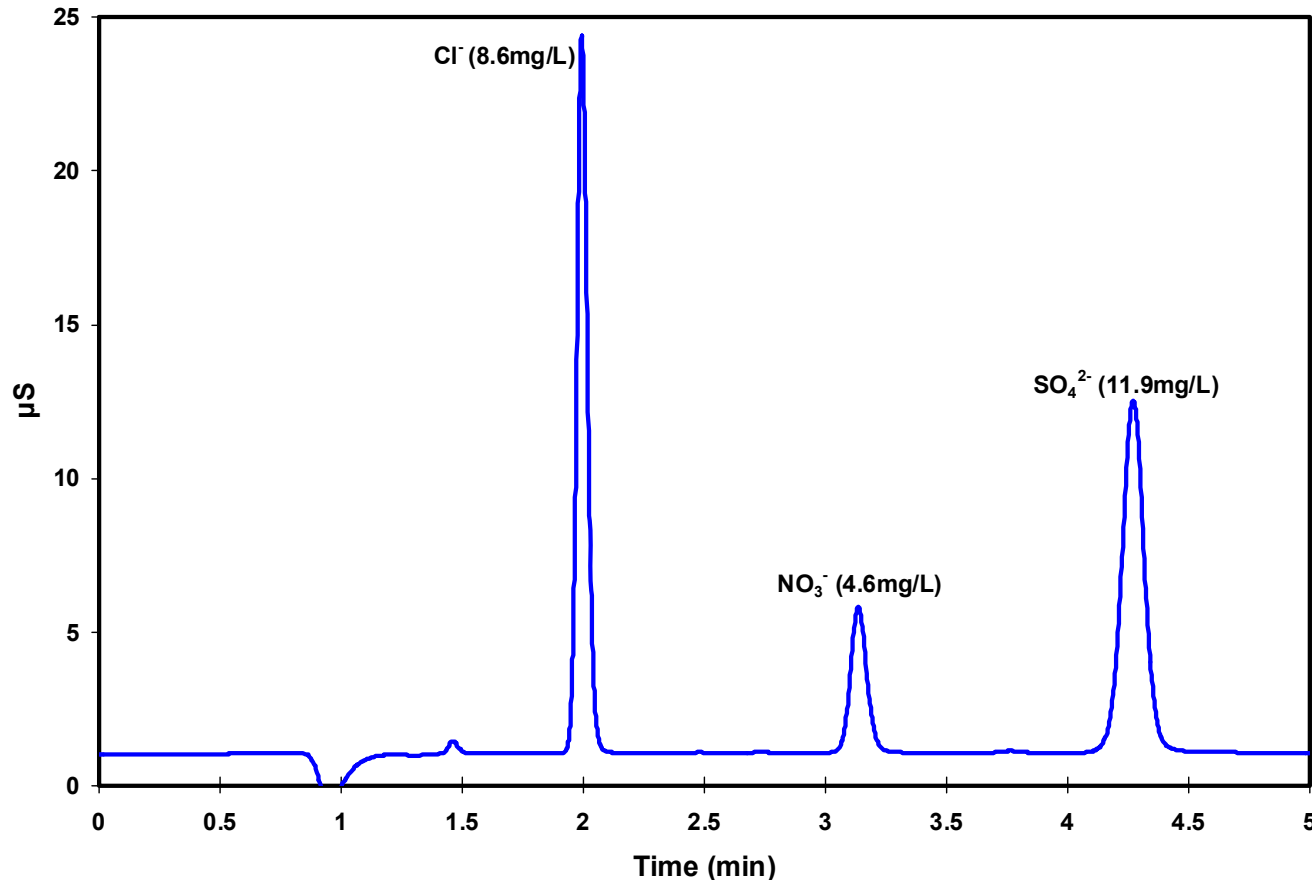## Figure 8: Analysis of environmental samples – River Water

Analysis conditions were the same as in figure 1.

Application to environmental samples

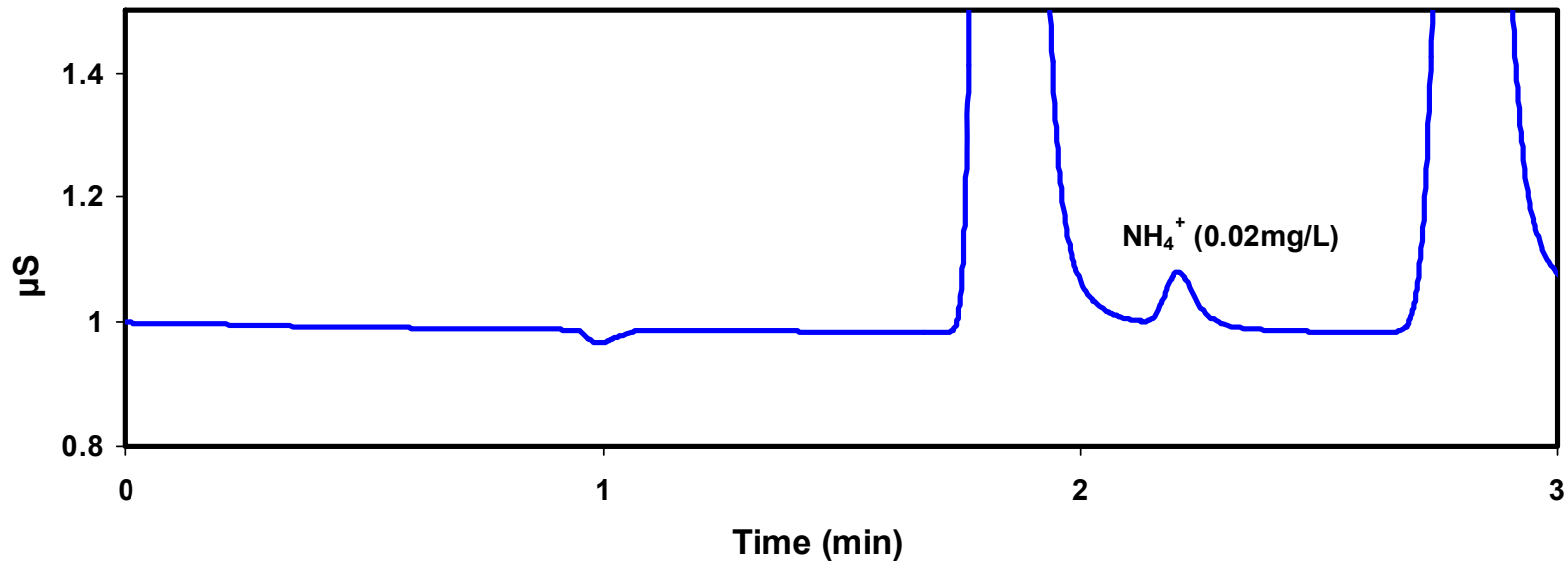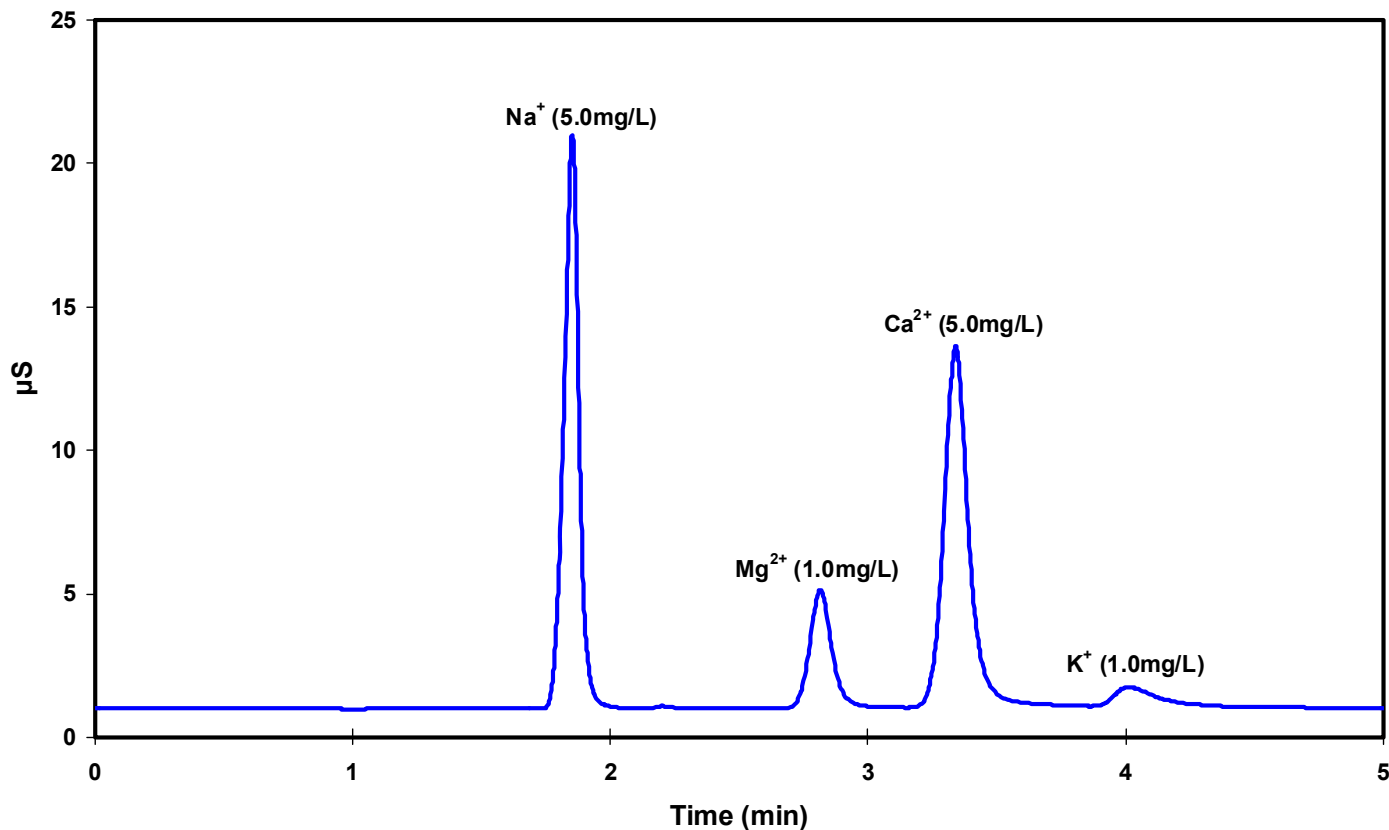## Figure 8: Analysis of environmental samples – River Water, cont.

Analysis conditions were the same as in figure 1.

Figure 9: Analysis of environmental samples – Simulated Tap Water

Analysis conditions were the same as in figure 2.

Figure 9: Analysis of environmental samples – Simulated Tap Water, cont.

Analysis conditions were the same as in figure 2.

Conclusions

- Common inorganic anions or cations could be analyzed in less than 5 minutes using TSKgel SuperIC-Anion HS or TSKgel SuperIC-Cation HS columns at a pressure below 20MPa.

- The TSKgel SuperIC-HS columns showed high resolution and well-balanced selectivity of common ions in an isocratic elution.

- Fast separation and detection by suppressed conductivity detection resulted in a wide dynamic range and highly sensitive detection of ions.

- As the TSKgel SuperIC-Anion HS packings are made of hydrophilic porous resin, early eluting ions such as fluoride were well-separated from the water dip.

- TSKgel SuperIC-Anion HS consist of highly crosslinked packings that are resistant to eluents containing organic solvent.

- The elution of carbonate ions in samples sometimes interferes with the quantitative determination of nitrite and bromide ions. With the use of the new TSKgel SuperIC-Anion HS, the relative position of the carbonate ions could be controlled by adjusting column temperature.