Evaluation of a Novel High Throughput Analytical Column for Ion Chromatography

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Introduction

- Ion chromatography (IC) is a versatile and widely accepted HPLC 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 replaced 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 packed 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 IC-2010 ion chromatograph system (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-A HS, 4.6mm ID x 1cm

Instrumentation

Instrument: IC-2010 Ion Chromatograph (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 (Millipore).

Environmental samples were taken in our office (tap water) and from a neighborhood river.

Spiked tap water samples were created by adding commonly present anions to Milli-Q water at concentrations normally found in tap water.

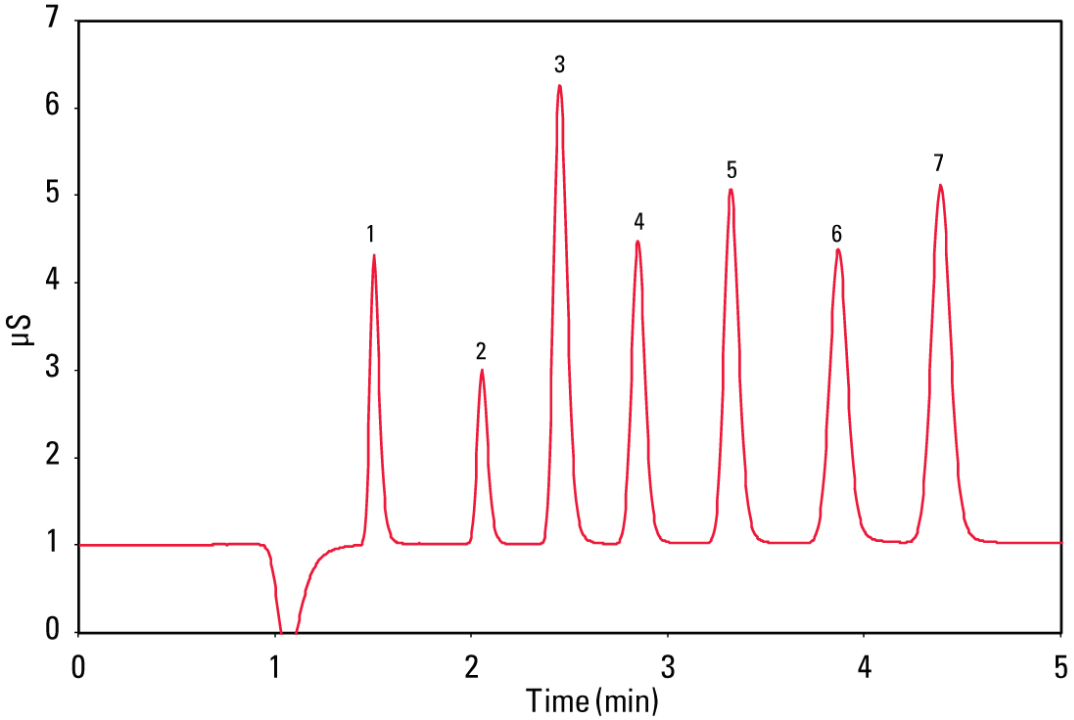
Separation of common ions on TSKgel SuperIC-Anion HS column

Table 1: Specifications of TSKgel SuperIC-Anion HS column

	TSKgel SuperIC-Anion HS
Part No.	0022766
Column size	4.6mm ID x 10cm
Container material	PEEK
Gel material	Porous hydrophilic polymer
Particle size	3.5µm
Functional group	Quaternary ammonium
Capacity	ca. 30meq/L-gel
Theoretical Plates (TP)	≥ 8,000 (SO_4^{2-})

Separation of common ions on TSKgel SuperIC-Anion HS column

Figure 1: Separation of 7 common anions

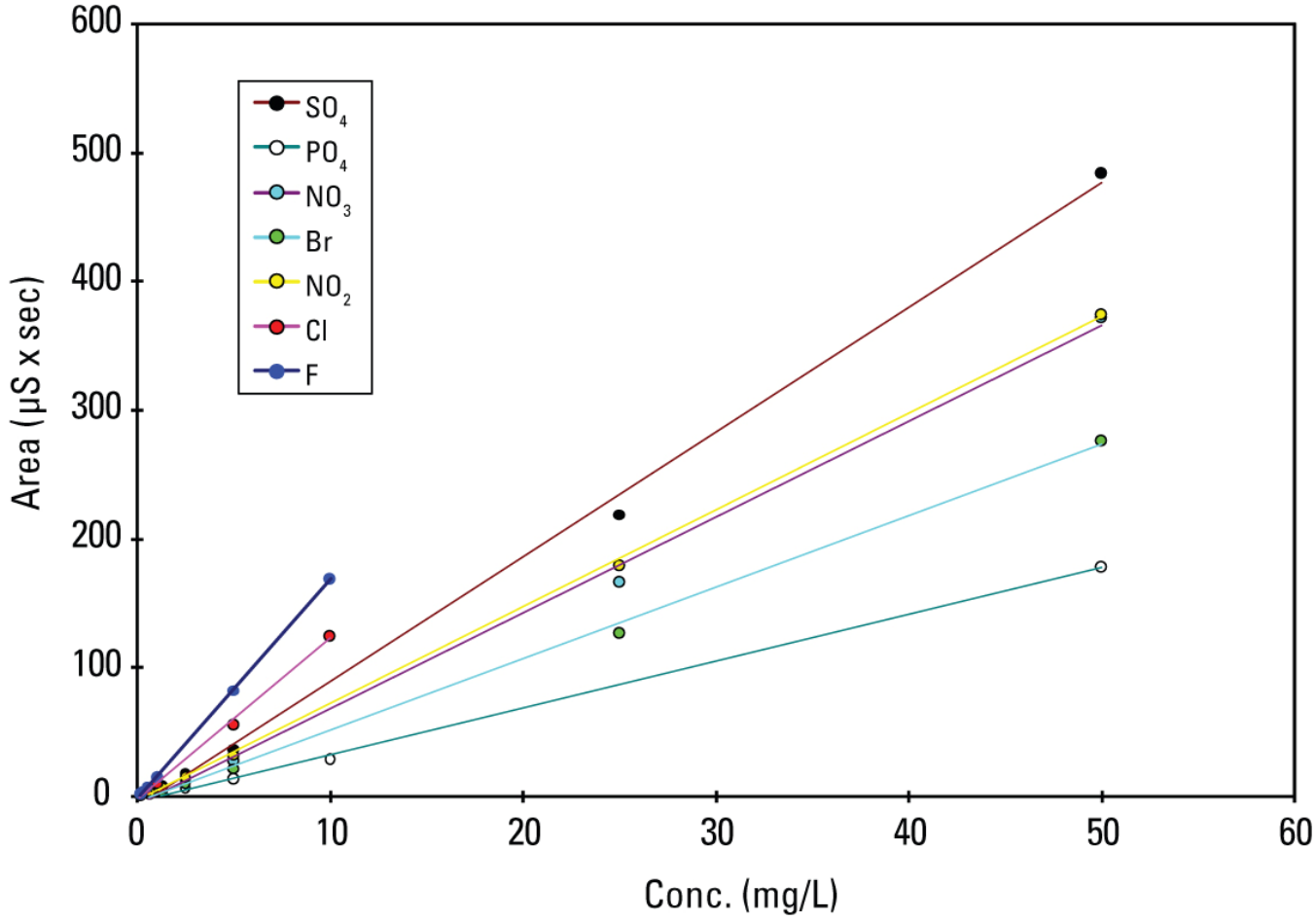


Columns:	TSKgel SuperIC-Anion HS, 4.6mm ID x 10cm TSKguardcolumn SuperIC-A HS, 4.6mm ID x 1cm
Mobile phase:	3.8mmol/L $NaHCO_3$ + 3.0mmol/L Na_2CO_3
Flow rate:	1.5mL/min
Detection:	Suppressed conductivity
Temperature:	40°C
Injection vol.:	30µL
Pressure:	16MPa
Suppressor gel:	TSKsuppress IC-A
Samples:	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)

Common inorganic anions were analyzed in less than 5 minutes at a pressure below 20MPa.

Separation of common ions on TSKgel SuperIC-Anion HS column

Figure 2: Calibration curve of each ion



Separation of common ions on TSKgel SuperIC-Anion HS column

Table 2: Limit of Detection of selected anions

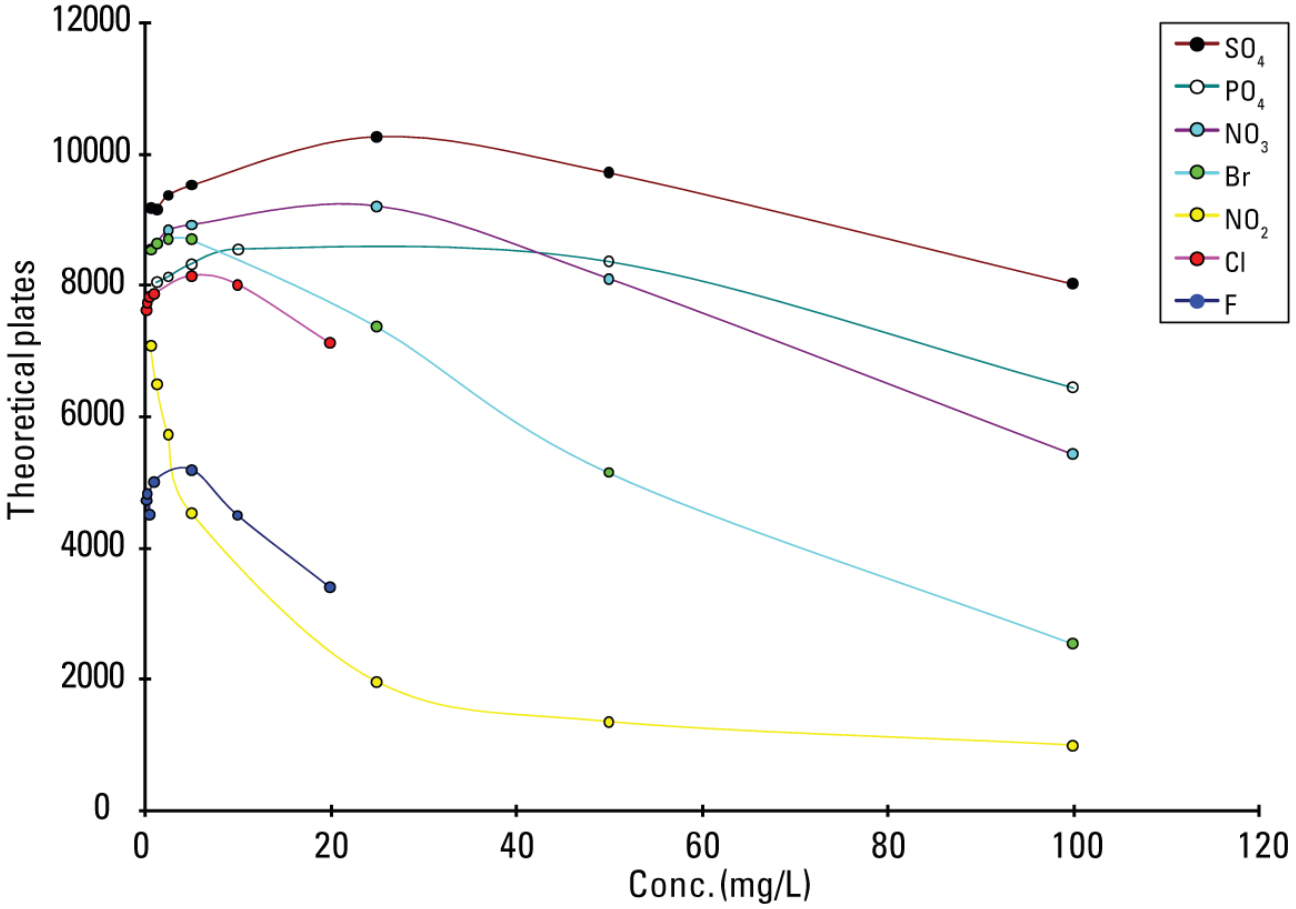
Anions	F^-	Cl^-	NO_2^-	Br^-	NO_3^-	PO_4^{3-}	SO_4^{2-}
(µg/L)	0.8	1.3	2.9	3.9	3.5	8.2	3.4

Analysis conditions as in Figure 1.

Limit of Detection (LOD) was calculated from S/N = 3

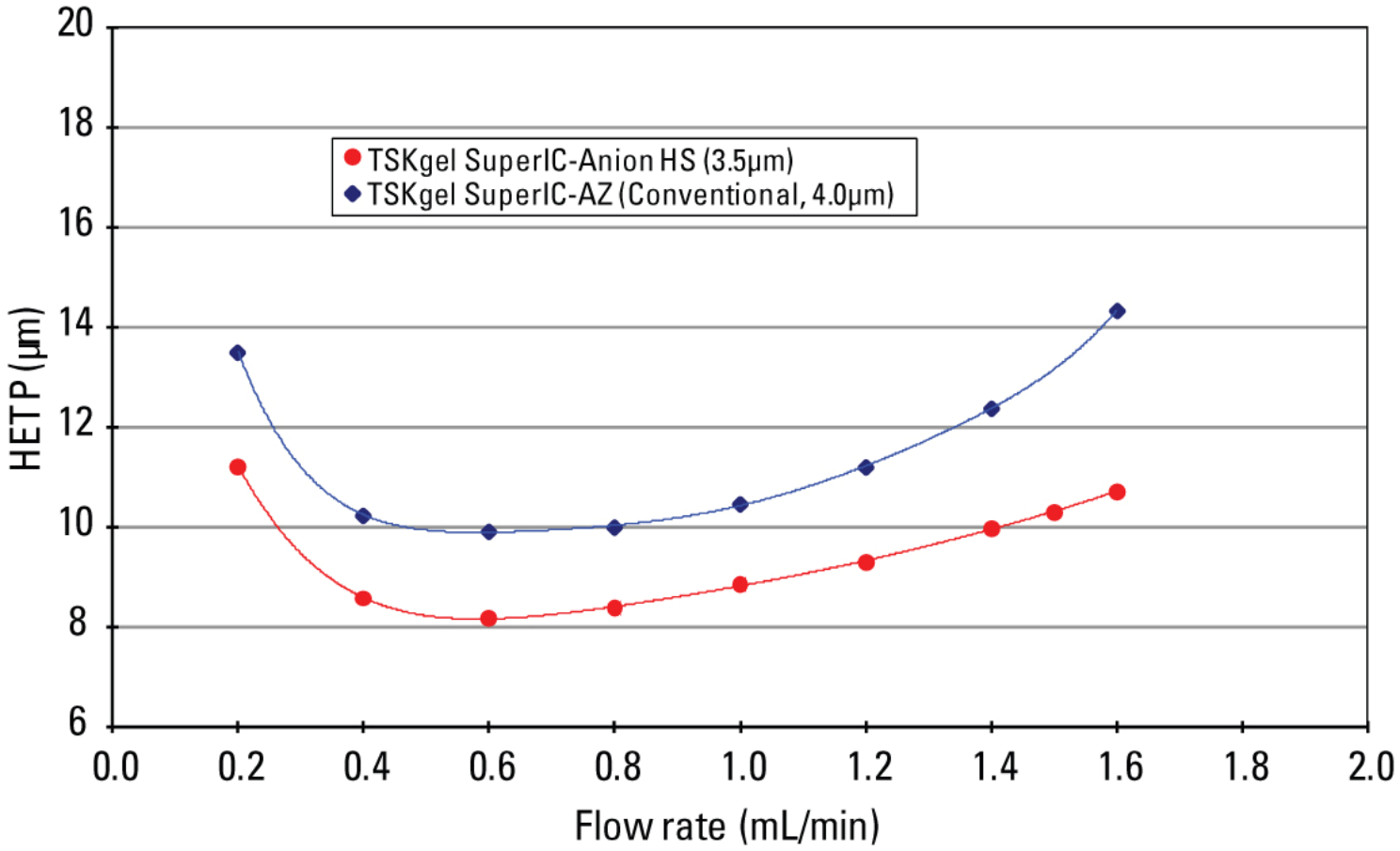
Evaluation of basic characteristics of TSKgel SuperIC-Anion HS column

Figure 3: Estimation of loadability



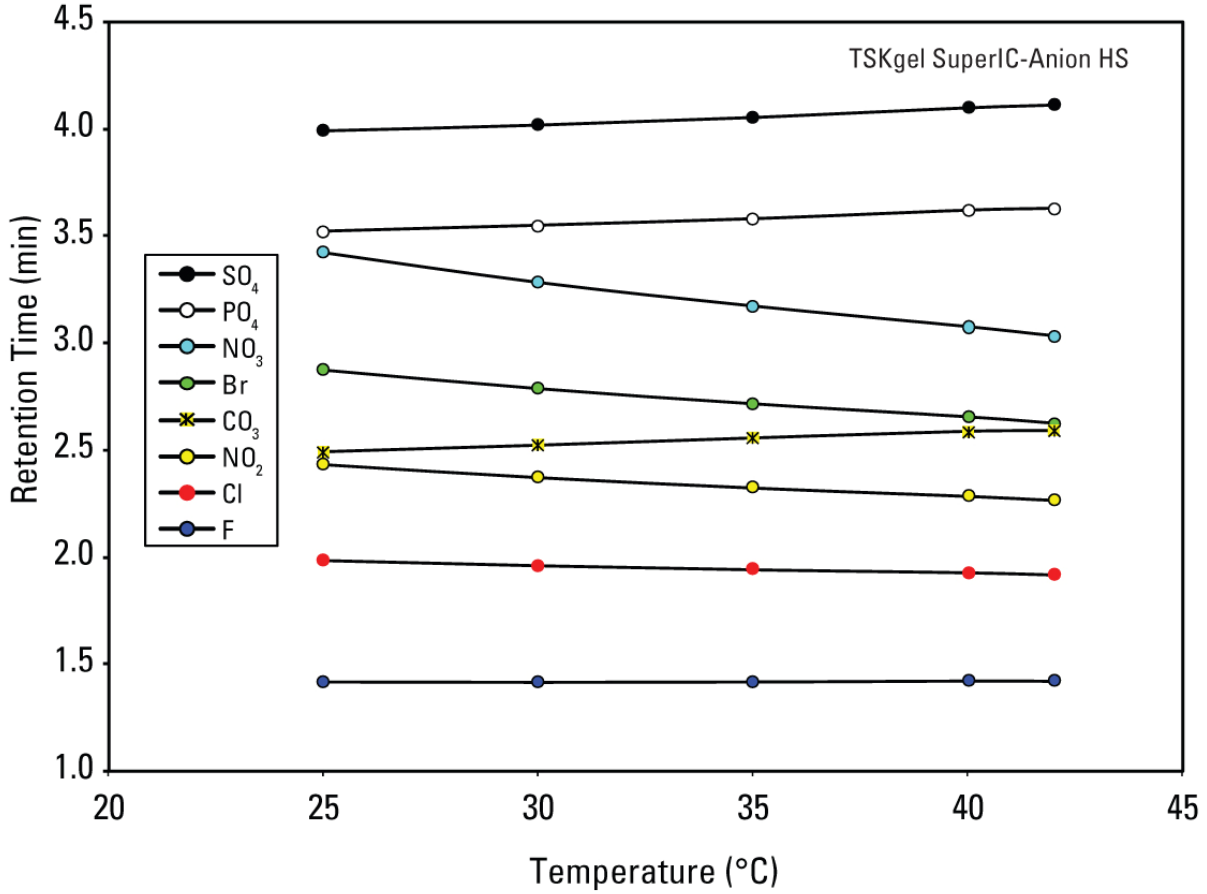
Evaluation of basic characteristics of TSKgel SuperIC-Anion HS column

Figure 4: Estimation of Van Deemter curves



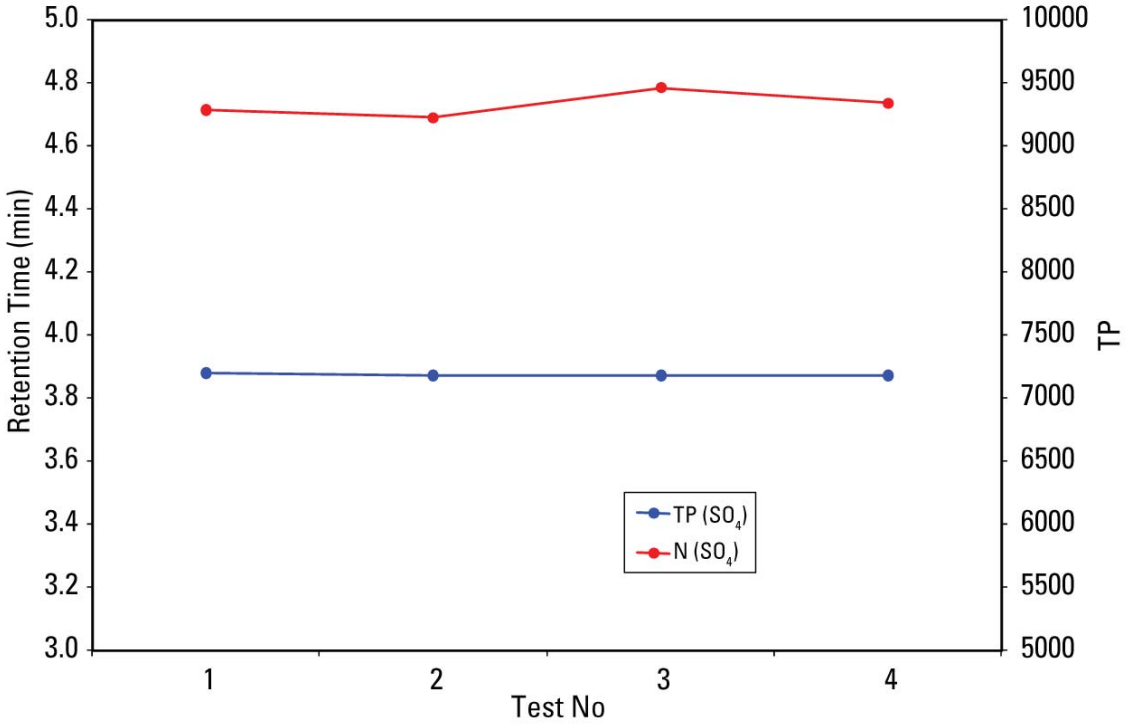
Evaluation of basic characteristics of TSKgel SuperIC-Anion HS column

Figure 5: Retention behavior of ions as a function of column temperature



Evaluation of basic characteristics of TSKgel SuperIC-Anion HS column

Figure 6: Effect of organic solvents on retention and efficiency of TSKgel SuperIC-Anion HS column



Test 1: evaluation of initial performance

Test 2: after ACN flow (1.2mL/min, 3hrs)

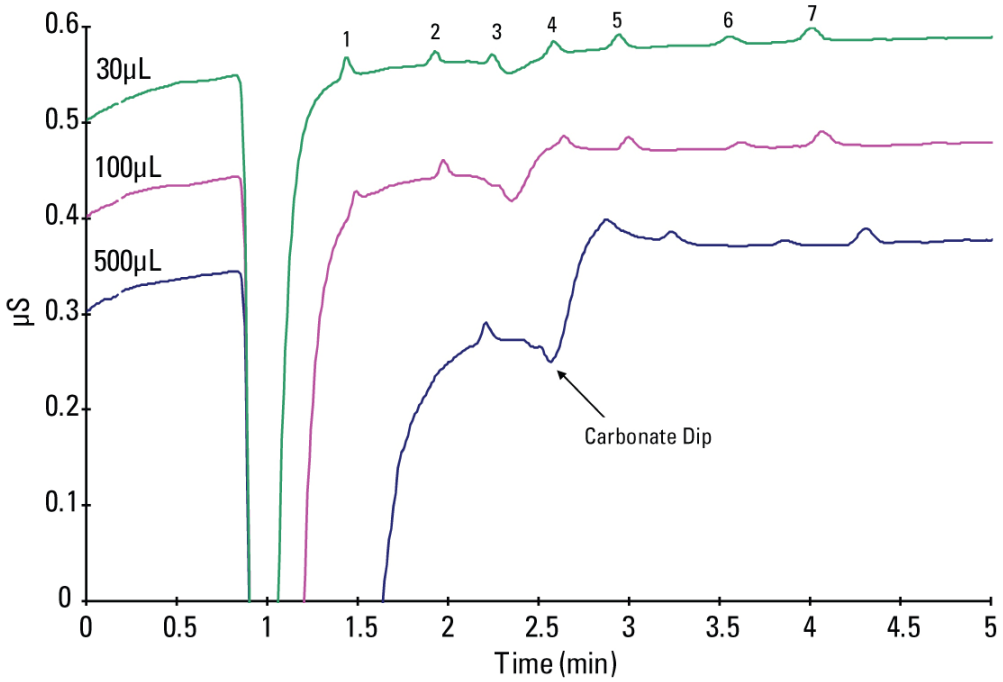
Test 3: after CH_3OH flow (1.2mL/min, 3hrs)

Test 4: after C_2H_5OH flow (0.8mL/min, 3hrs)

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

Carbonate dip control

Figure 7: Effect of injection volume using the analysis conditions described in Figure 1

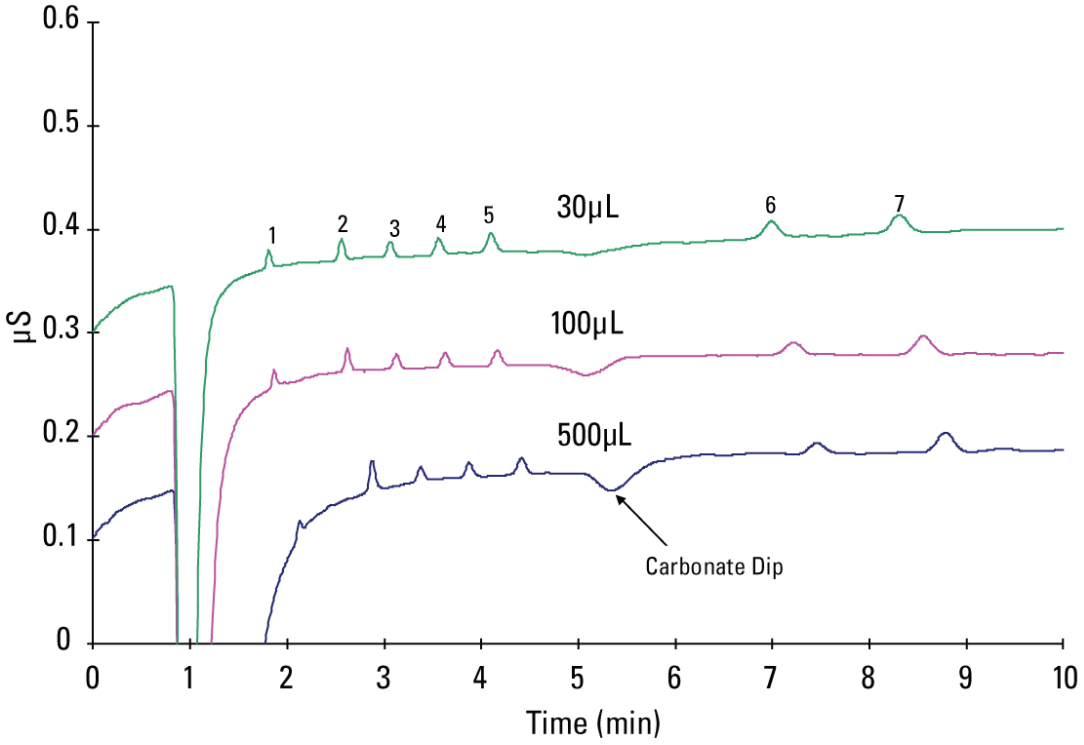


Peak No.	Anions	Concentration (µg/L)		
		30µL	100µL	500µL
1	F^-	5	1.25	0.25
2	Cl^-	5	1.25	0.25
3	NO_2^-	10	2.5	0.5
4	Br^-	15	3.75	0.75
5	NO_3^-	15	3.75	0.75
6	PO_4^{3-}	30	10	3.0
7	SO_4^{2-}	15	3.75	0.75

The carbonate dip interferes with the detection of nitrite and bromide ions. Alternate mobile phase conditions were investigated to prevent the carbonate dip from interfering with the analysis (see Figures 8 & 9).

Carbonate dip control

Figure 8: Effect of injection volume after adjusting the mobile phase conditions (see also Figure 9).

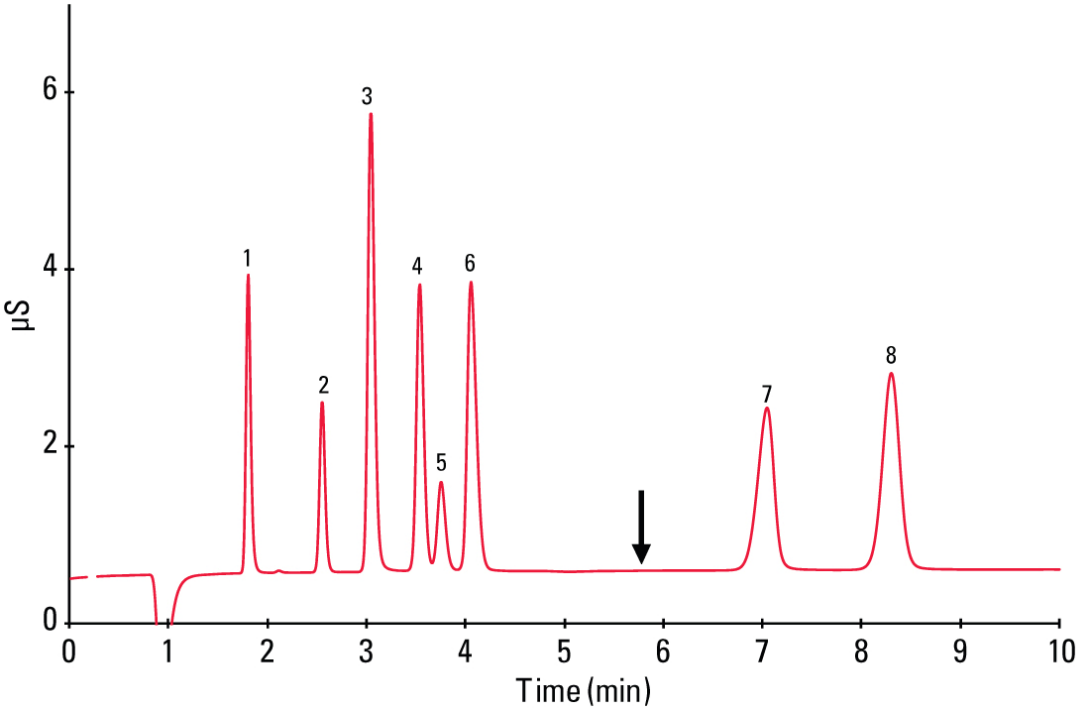


Peak No.	Anions	Concentration (µg/L)		
		30µL	100µL	500µL
1	F^-	5	1.25	0.25
2	Cl^-	5	2.5	0.5
3	NO_2^-	15	3.75	0.75
4	Br^-	25	6.25	1.25
5	NO_3^-	25	6.25	1.25
6	PO_4^{3-}	100	25	5.0
7	SO_4^{2-}	40	10	2.0

Optimized mobile phase composition allows the resolution of all of the anions in this study.

Carbonate dip control

Figure 9: Optimized conditions for large volume injection using a TSKgel SuperIC-Anion HS column

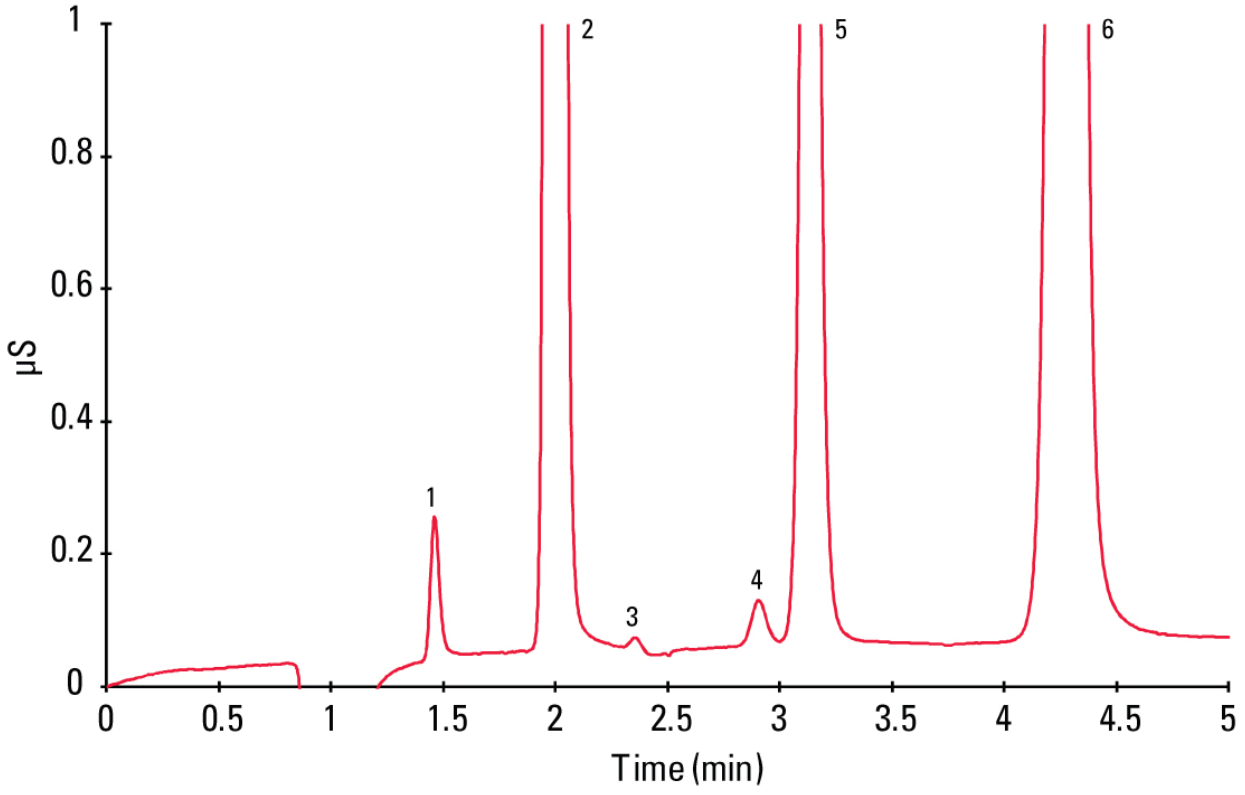


Columns:	TSKgel SuperIC-Anion HS, 4.6mm ID x 10cm TSKguardcolumn SuperIC-A HS, 4.6mm ID x 1cm
Mobile phase:	7.5mmol/L $NaHCO_3$ + 0.8mmol/L Na_2CO_3
Flow rate:	1.5mL/min
Detection:	Suppressed conductivity
Temperature:	40°C
Injection vol.:	30µL
Pressure:	16MPa
Suppressor gel:	TSKsuppress IC-A
Samples:	1. fluoride (1mg/L) 2. chloride (1mg/L) 3. nitrite (5mg/L) 4. bromide (5mg/L) 5. chlorate (2mg/L) 6. nitrate (10mg/l) 7. phosphate (10mg/L) 8. sulfate (5mg/L)

Optimized mobile phase composition allows the resolution of all of the anions in this study.

Trace analysis of nitrite ion

Figure 10: Analysis of spiked tap water

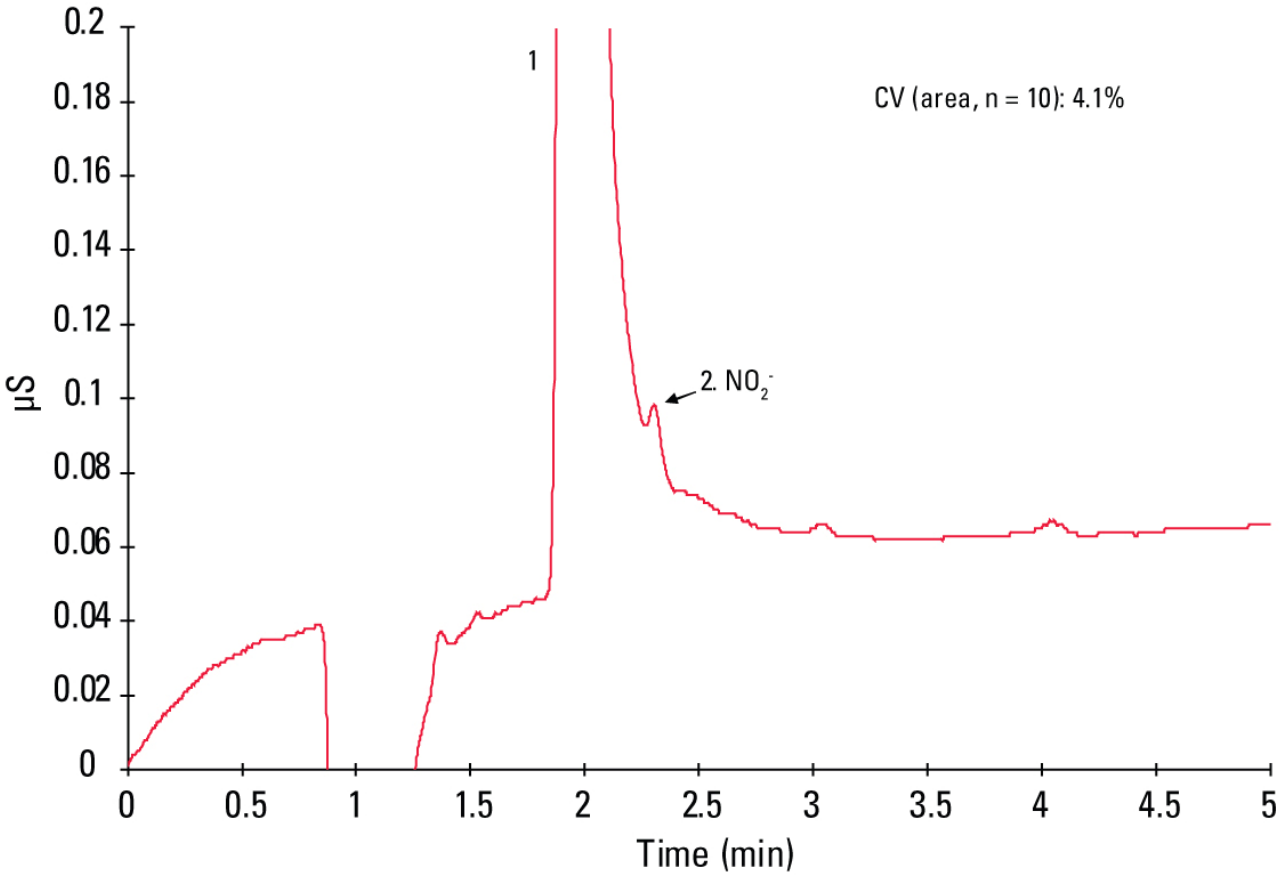


Analysis conditions as in Figure 1.

Peaks:
1. fluoride (0.05mg/L)
2. chloride (10mg/L)
3. nitrite (0.005mg/L as NO_2-N)
4. chlorate (0.1mg/L)
5. nitrate (3mg/L)
6. sulfate (10mg/L)

Trace analysis of nitrite ion

Figure 10A: Analysis of spiked tap water

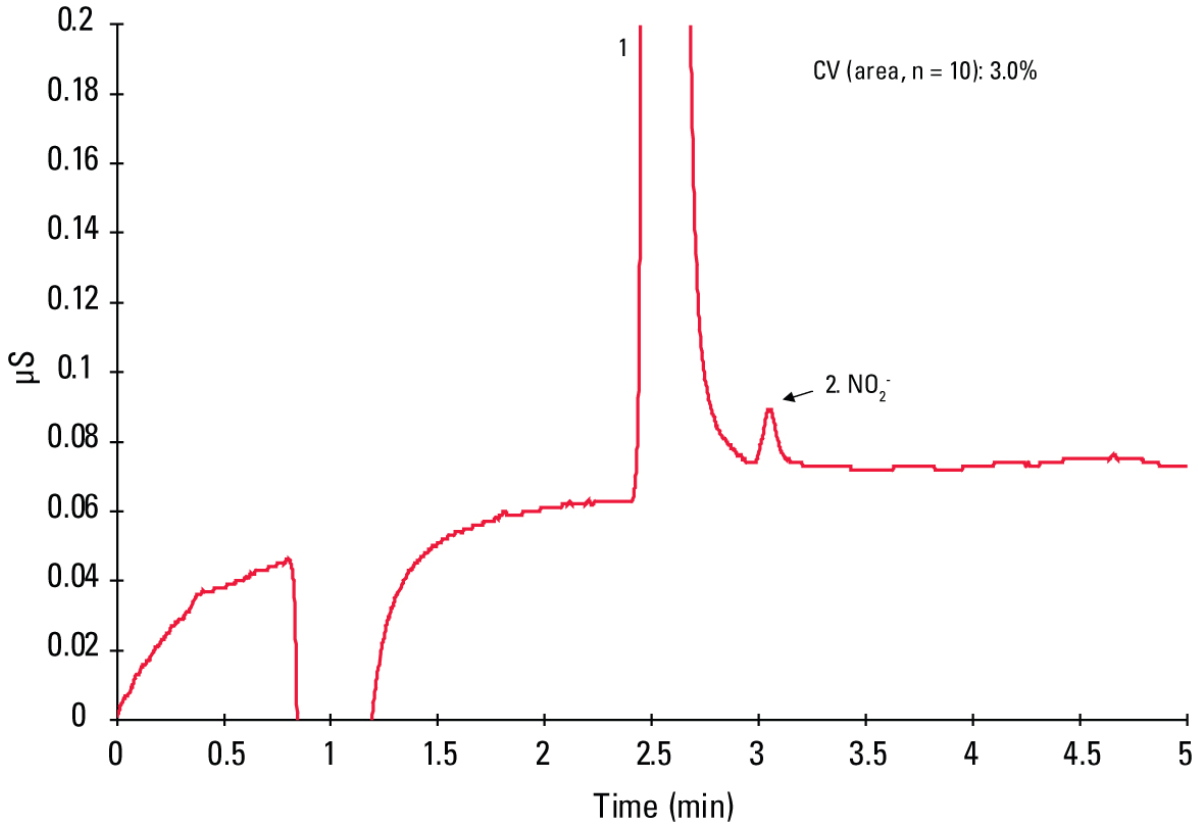


Analysis conditions as in Figure 1.

Peaks: 1. chloride (30mg/L)
2. nitrite (0.005mg/L as NO_2-N)

Trace analysis of nitrite ion

Figure 10B: Analysis of spiked tap water



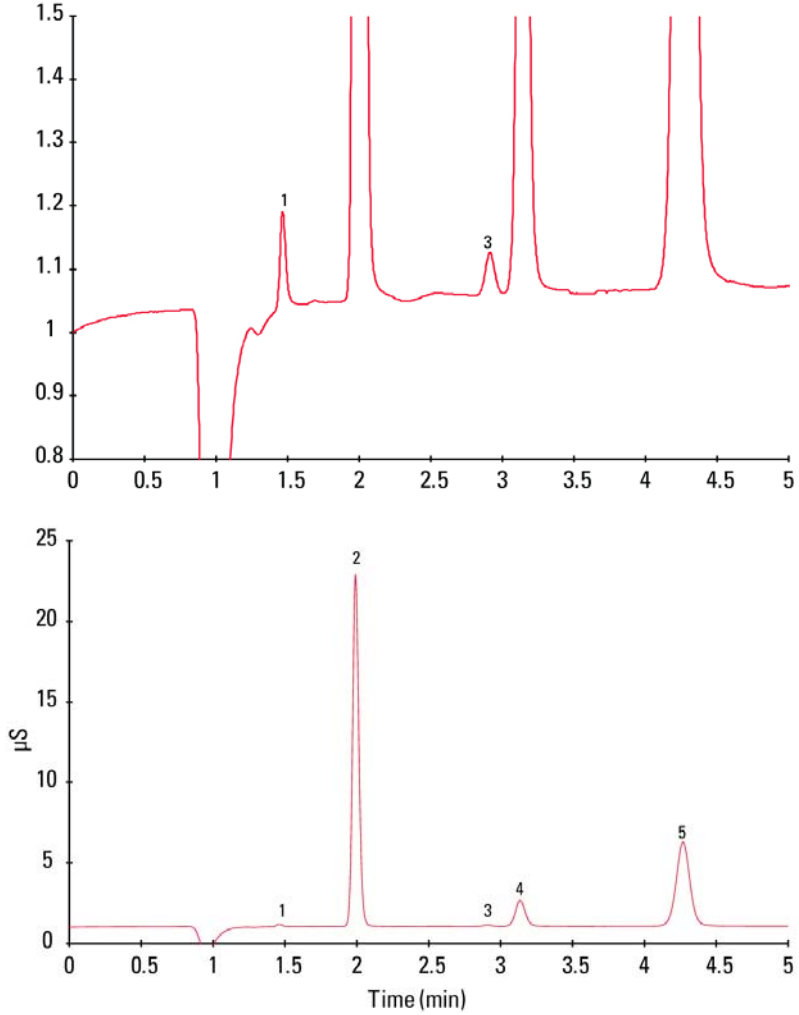
Analysis conditions as in Figure 9.

Peaks: 1. chloride (30mg/L)
2. nitrite (0.005mg/L as NO_2-N)

Optimized mobile phase composition allows a better separation of nitrite and chloride.

Application to environmental samples

Figure 11: Analysis of tap water

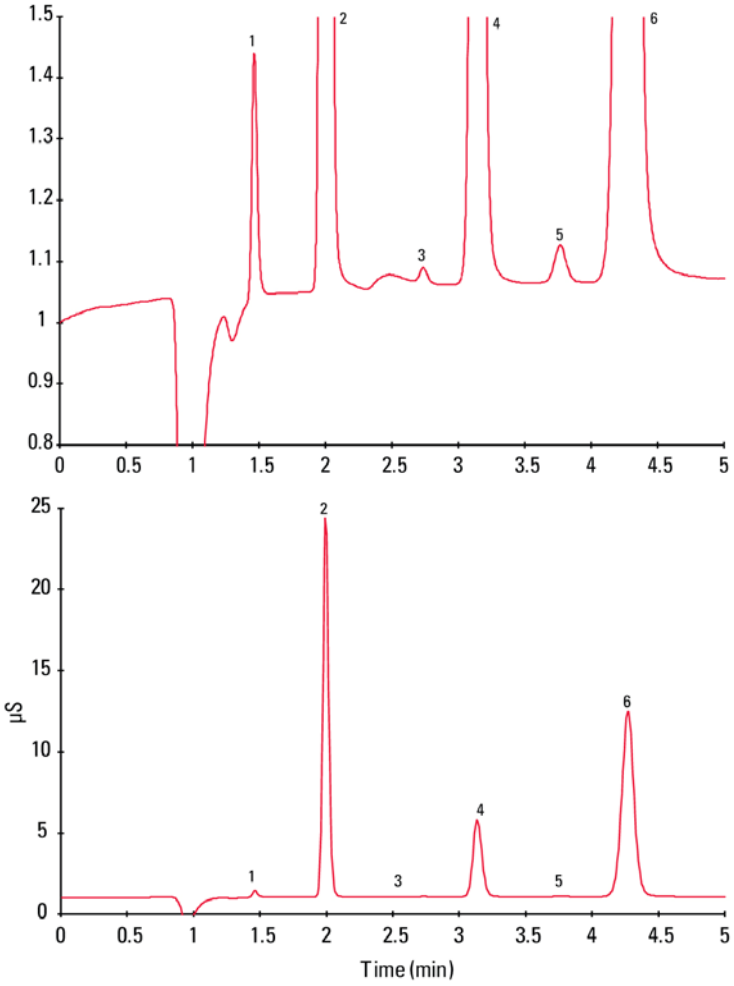


Analysis conditions as in Figure 1.

Peaks: 1. fluoride (0.036mg/L)
2. chloride (7.92mg/L)
3. chlorate (0.089mg/L)
4. nitrate (1.58mg/L)
5. sulfate (5.48mg/L)

Application to environmental samples

Figure 12: Analysis of river water

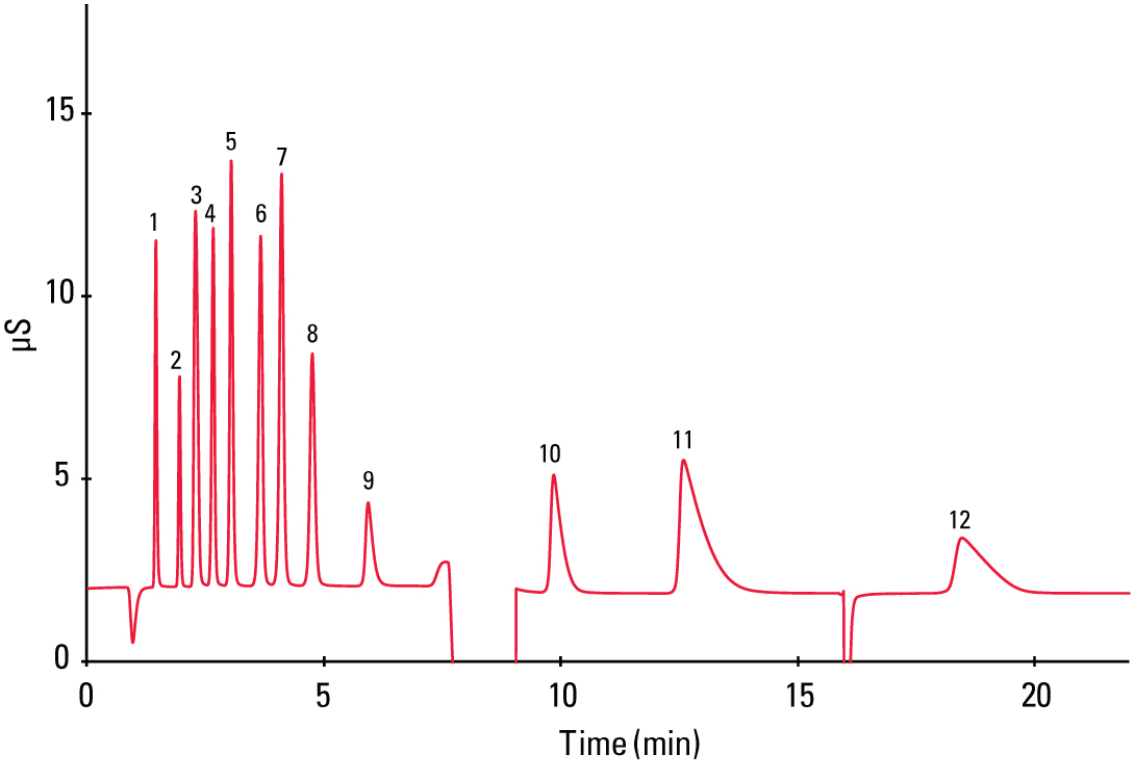


Analysis conditions as in Figure 1.

Peaks: 1. fluoride (0.094mg/L)
2. chloride (8.59mg/L)
3. bromide (0.024mg/L)
4. nitrate (4.61mg/L)
5. phosphate (0.061mg/L)
6. sulfate (11.9mg/L)

Stepwise gradient analysis using IC-2010

Figure 13: Separation of various anions



Columns:	TSKgel SuperIC-Anion HS, 4.6mm ID x 10cm TSKguardcolumn SuperIC-A HS, 4.6mm ID x 1cm
Mobile phase:	A. 3.8mmol/L $NaHCO_3$ + 3.0mmol/L Na_2CO_3 B. 4.5mmol/L $NaHCO_3$ + 3.5mmol/L Na_2CO_3 + 10% ACN
Flow rate:	1.3 - 1.5mL/min
Detection:	Suppressed conductivity
Temperature:	40°C
Injection vol.:	30µL
Pressure:	14MPa
Suppressor gel:	TSKsuppress IC-A
Samples:	1. fluoride (2mg/L) 2. chloride (2mg/L) 3. nitrite (10mg/L) 4. bromide (10mg/L) 5. nitrate (10mg/L) 6. phosphate (20mg/L) 7. sulfate (10mg/L) 8. oxalate (10mg/L) 9. thiosulfate (10mg/L) 10. thiocyanate (40mg/L) 11. perchlorate (50mg/L)

Gradient profile

Time (min)	B(%)	Flow rate	Remarks
0	0%	1.5	gradient start
6.0	100%	1.5	
6.5	100%	1.3	
8.5	100%	1.3	suppressor valve change
16.5	100%	1.3	suppressor valve change
20	0%	1.5	
25	0%	1.5	next injection

Conclusions

- Common inorganic anions could be analyzed in less than 5 minutes using a TSKgel SuperIC-Anion HS column at a pressure below 20MPa.
- The TSKgel SuperIC-Anion HS column 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 are well separated from the water dip.
- TSKgel SuperIC-Anion HS consist of a highly crosslinked packing that is 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 column, the relative position of the carbonate ions could be controlled by adjusting the eluent composition.
- Optimization of mobile phase conditions provided better separation of nitrite and chloride ions at trace levels.