TOSOH

No.107

SEPARATION REPORT

TSKgel SuperIC Columns for High-Performance Ion Chromatography

— Contents —

1. Introduction

Ion chromatography (IC) is an analytical technique that is employed in a variety of fields, including environmental and food sciences, chemistry, pharmaceutical development, and mining, to simultaneously separate and quantify multiple inorganic ions with ease. Three types of separation modes are used: ion exchange chromatography; ion exclusion chromatography; and ion-pair reversed-phase chromatography. The ion exchange mode is frequently utilized because it can be used with many types of ions and separation can be adjusted easily. Conductometric detection, which detects changes in electrical conductivity, is the most commonly used method of detection, but with ions that have absorption in the UV region, such as nitrate, nitrite, and iodide ions, ion identification is facilitated by conductometric detection together with UV absorbance detection. With conductometric detection, the conductivity of the eluent becomes the background. As a result, eluents that can be used with a non-suppressor IC are limited. However, in suppressor IC, because detection is performed after reducing conductivity of the eluate from the column, not only are the restrictions on the eluents that can be used alleviated, but also ions can be detected with a high sensitivity. The TSKgel SuperIC columns include a variety of packed columns for both suppressor IC and non-suppressor IC. Here, the basic characteristics and applications of the TSKgel SuperIC columns for IC are introduced. **Table 1** shows the specifications and characteristics of each packed column.

2. Columns for anion analysis

2-1.TSKgel SuperIC-AZ

TSKgel SuperIC-AZ is a column for anion analysis using the suppressor method, in which a carbonate buffer is used as the eluent. The packing material comprises hydrophilic polymer gel (particle size: 4 µm) to which a quaternary ammonia group has been introduced. By altering the composition of the carbonate buffer, various types of ions can be separated. In addition, because the mechanical strength of the base material is high and there is little shrinkage or swelling of the packing material in response to changes in solvent, organic solvents can be added to the eluent. Adding an organic solvent to the eluent enables the rapid elution of strongly hydrophobic ions, which have long retention times. In addition, contaminants that adhere to the column during the measurement of real samples can be removed by washing with an organic solvent.

2-1-1. Separation of standard anions

In addition to the 7 standard anions, a variety of other ions can also be separated well with the TSKgel SuperIC-AZ, depending on the composition of the carbonate buffer or by adding an organic solvent. **Table 2** shows the composition of representative eluents; and **Figures 1** through **3** show chromatograms of standard anions produced with each eluent.

1) Standard separation conditions
   Seven standard anions can be analyzed in approximately 15 minutes. These are the standard elution conditions with the broadest range of application.
2) High resolution separation conditions
   These can improve the separation of rapidly eluting ions (fluoride ions, oxidative halogen acid ions**[Please confirm this term]**, organic acid ions).
3) Hydrophobic anions separation conditions
   These are effective separation conditions for the analysis of anions, including hydrophobic anions that elute slowly (iodide ions, thiocyanate ions, thiosulfate ions, etc.). Using an eluent that contains an organic solvent (23% acetonitrile) causes hydrophobic ions to elute rapidly, decreasing the analysis time.

Table 1 Characteristics of the TSKgel SuperIC columns of packing materials

Product name	TSKgel SuperIC-AZ	TSKgel SuperIC-Anion	TSKgel SuperIC-AP	TSKgel SuperIC-CR	TSKgel SuperIC-A/C
Product No.	0021444	0019673	0019840 (15 cm), 0019841 (7.5 cm)	0021475	0019843
Column size	4.6 mm I.D.x 15 cm (PEEK*1)	4.6 mm I.D.x 15 cm (PEEK*1)	4.6 mm I.D.x 15 cm (PEEK*1) 4.6 mm I.D.x 7.5 cm (PEEK*1)	4.6 mm I.D.x 15 cm (PEEK*1)	6.0 mm I.D.x 15 cm (SUS316)
Base material	Hydrophilic polymer	Polystyrene	Hydrophilic polymer	Polystyrene	Hydrophilic polymer
Particle size	4 µm	5 µm	6 µm	3 µm	4 µm
Functional group	Quaternary ammonium group	Quaternary ammonium group	Quaternary ammonium group	Carboxyl group	Carboxyl group
Ion exchange capacity	Approx. 30 meq/L	Approx. 12 meq/L	Approx. 30 meq/L	≥ 1.0 eq/L	Approx. 0.2 eq/L
Counterion	Carbonate ion	Borate, carbonate ions	Carbonate ion	Hydrogen ion	Hydrogen ion
Shipping solvent	Solvent for inspection*2	Solvent for inspection *2	Solvent for inspection *2	Solvent for inspection *2	H_2O
Application	Anion analysis	Anion analysis	Anion analysis	Cation analysis	Cation/anion simultaneous analysis

*1: Column member: PEEK (SuperIC-A/C: SUS316)
*2: Solvent for inspection :
TSKgel SuperIC-AZ: 1.9 mmol/L sodium hydrogen carbonate + 3.2 mmol/L sodium carbonate
TSKgel SuperIC-Anion: 6.0 mmol/L sodium tetraborate + 15 mmol/L boric acid + 0.2 mmol/L sodium hydrogen carbonate
TSKgel SuperIC-AP: 1.7 mmol/L sodium hydrogen carbonate + 1.8 mmol/L sodium carbonate
TSKgel SuperIC-CR: 2.2 mmol/L methanesulfonic acid

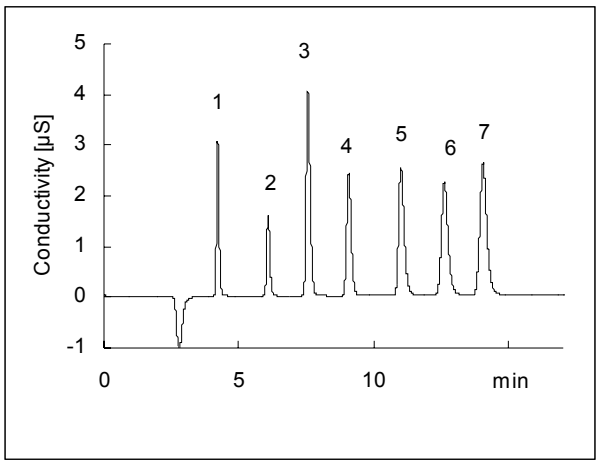

Figure 1 Separation of standard anions

(standard separation conditions)

Column:	TSKgel SuperIC-AZ (4.6 mm I.D. × 15 cm)	
Eluent:	1.9 mmol/L $NaHCO_3$ + 3.2 mmol/L Na_2CO_3	
Flow rate:	0.8 mL/min	
Detection:	Conductometric	
Temperature:	40 °C	
Suppressor gel:	TSKsuppressIC-A	
Samples:	1. F^- (1 mg/L)	2. Cl^- (1 mg/L)
	3. NO_2^- (5 mg/L)	4. Br^- (5 mg/L)
	5. NO_3^- (5 mg/L)	6. HPO_4^{2-} (10 mg/L)
	7. SO_4^{2-} (5 mg/L)	
Injection volume:	30 µL	

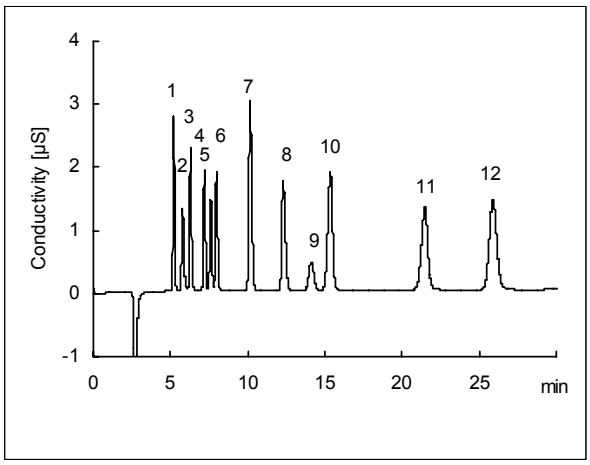

Figure 2 Separation of standard anions

(precision separation conditions)

Column:	TSKgel SuperIC-AZ (4.6 mm I.D. × 15 cm)	
Eluent:	7.5 mmol/L $NaHCO_3$ + 1.1 mmol/L Na_2CO_3	
Flow rate:	0.8 mL/min	
Detection:	Conductometric	
Temperature:	40 °C	
Suppressor gel:	TSKsuppressIC-A	
Samples:	1. F^- (1 mg/L)	2. $CH_3CO_2^-$ (10 mg/L)
	3. HCO_2^- (3 mg/L)	4. ClO_2- (3 mg/L)
	5. BrO_3^- (4 mg/L)	6. Cl^- (1 mg/L)
	7. NO_2^- (5 mg/L)	8. Br^- (5 mg/L)
	9. ClO_3^- (2 mg/L)	10. NO_3^- (5 mg/L)
	11. HPO_4^{2-} (10 mg/L)	12. SO_4^{2-} (5 mg/L)
Injection volume:	30 µL	

Table 2 List of separation conditions (TSKgel SuperIC-AZ)

Eluent:	Standard: 1.9 mmol/L $NaHCO_3$ + 3.2 mmol/L Na_2CO_3
	High resolution: 7.5 mmol/L $NaHCO_3$ + 1.1 mmol/L Na_2CO_3
	Hydrophobic anions (1.9 mmol/L $NaHCO_3$ + 3.2 mmol/L Na_2CO_3) in H_2O/CH_3CN = 77/23 (v/v)
Flow rate:	Standard, high resolution: 0.8 mL/min
	Hydrophobic anions: 0.6 mL/min
Detection:	Conductometric
Column temperature:	40 °C
Injection volume:	30 µL
Suppressor gel:	TSKsuppressIC-A

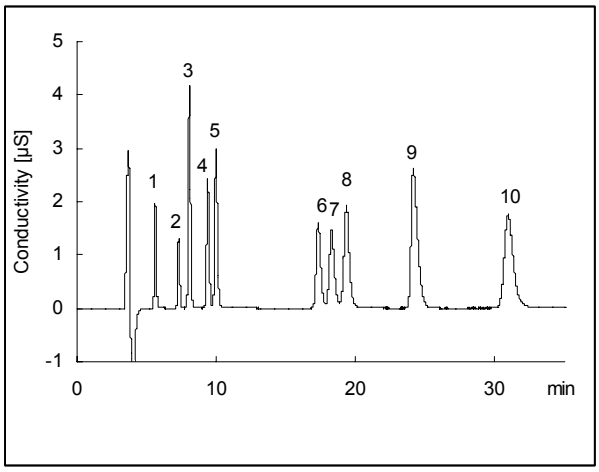

Figure 3 Separation of hydrophobic anions (Hydrophobic anions separation conditions)

Column:	TSKgel SuperIC-AZ (4.6 mm I.D. × 15 cm)
Eluent:	(1.9 mmol/L $NaHCO_3$ + 3.2 mmol/L Na_2CO_3) in H_2O/CH_3CN = 77/23 (v/v)
Flow rate:	0.6 mL/min
Detection:	Conductometric
Temperature:	40 °C
Suppressor gel:	TSKsuppressIC-A
Samples:	1. F^- (1 mg/L) 2. Cl^- (1 mg/L) 3. NO_2^- (5 mg/L) 4. Br^- (5 mg/L) 5. NO_3^- (5 mg/L) 6. I^- (10 mg/L) 7. HPO_4^{3-} (10 mg/L) 8. SO_4^{2-} (5 mg/L) 9. SCN^- (10 mg/L) 10. $S_2O_3^{2-}$ (10 mg/L)
Injection volume:	30 µL

2-1-2. Flow rate dependence

Theoretical plates are one index of column performance. Theoretical plates vary depending on each of the analytical parameters but are markedly dependent on the flow rate (van Deemter equation). **Figure 4** shows the relationship between flow rate and height equivalent to a theoretical plate (HETP) for sulfide ions under standard separation conditions. Although behaviors will vary slightly depending on the ion species, HETP is clearly minimal with the TSKgel SuperIC-AZ (column efficiency is high) and resolution is best at a flow rate of 0.6-0.8 mL/min.

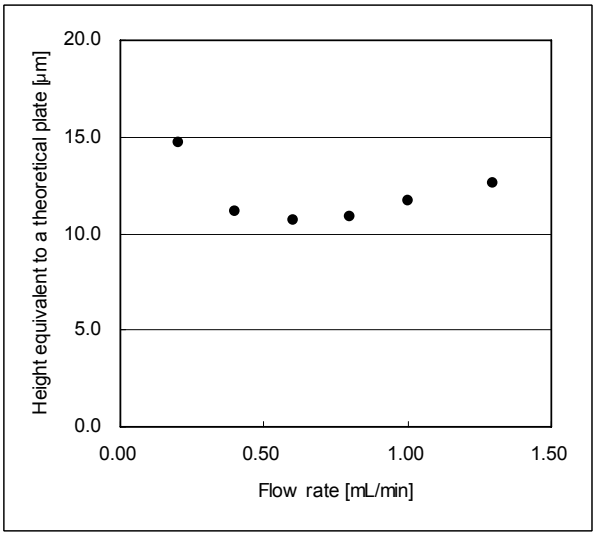

Figure 4 Flow rate dependence of column efficiency

Column:	TSKgel SuperIC-AZ (4.6 mm I.D. × 15 cm)
Eluent:	(1.9 mmol/L $NaHCO_3$ + 3.2 mmol/L Na_2CO_3) in H_2O/CH_3CN = 77/23 (v/v)
Flow rate:	0.2-1.3 mL/min
Detection:	Conductometric
Temperature:	40°C
Suppressor gel:	TSKsuppressIC-A
Sample:	SO_4^{2-} (10 mg/L)
Injection volume:	30 µL

2-1-3. Analysis of trace anions

1) Applications for analyzing trace quantities of 7 standard anions

Figure 5 shows a chromatogram of μg/L levels of anions. The repeatability of this analysis is shown in **Table 3**. At n = 10, the relative standard deviation (RSD) was ≤0.2% for retention time, and ≤10% for peak area, indicating good repeatability of analysis.

2) Application of trace nitite (NO_2) ions

Trace NO_2 ions, which elute close to surplus chloride ions, are analyzed as an index of resolution and detection sensitivity in anion analysis. **Figure 6** shows a chromatogram of an actual concentration of nitrite ions (0.005 mg/L in the form of nitrite-nitrogen (NO_2-N)) in a sample containing 30 mg/L of chloride ions. Trace nitrite ions could be determined with good repeatability, unaffected by the coexistence of chloride ions, as the relative standard deviation measured for peak area was 4.7% (n=6).

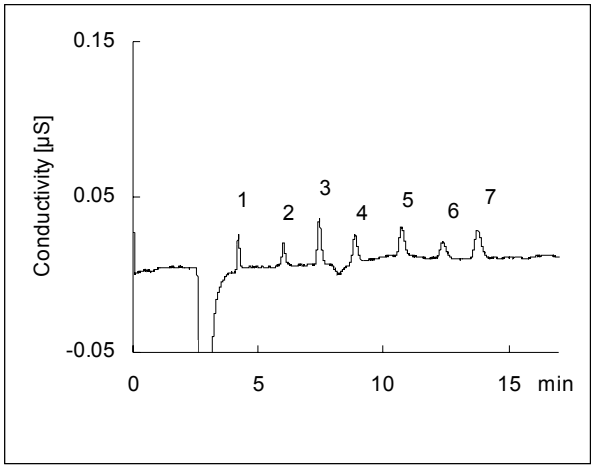

Figure 5 Chromatogram of trace ions

Column: TSKgel SuperIC-AZ (4.6 mm I.D. × 15 cm)
Eluent: 1.9 mmol/L $NaHCO_3$ + 3.2 mmol/L Na_2CO_3
Flow rate: 0.8 mL/min
Detection: Conductometric
Temperature: 40 °C
Suppressor gel: TSKsuppressIC-A
Samples: 1. F^- (8 μg/L) 2. Cl^- (8 μg/L)
3. NO_2^- (40 μg/L) 4. Br^- (40 μg/L)
5. NO_3^- (40 μg/L) 6. PO_4^{2-} (80 μg/L)
7. SO_4^{2-} (40 μg/L)
Injection volume: 30 μL

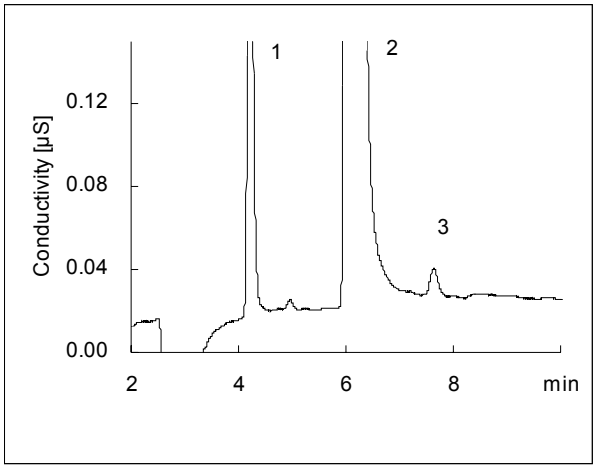

Figure 6 Chromatogram of trace NO_2 ions in high concentration of Cl

Column: TSKgel SuperIC-AZ (4.6 mm I.D. × 15 cm)
Eluent: 1.9 mmol/L $NaHCO_3$ + 3.2 mmol/L Na_2CO_3
Flow rate: 0.8 mL/min
Detection: Conductometric
Temperature: 40 °C
Suppressor gel: TSKsuppressIC-A
Samples: 1. F^- (0.1 mg/L)
2. Cl^- (301 mg/L)
3. NO_2^- (0.0051 mg/L, NO_2^- N)
Injection volume: 30 μL

Table 3 Repeatability of analysis of trace anions

	Injection volume: 30 μL n = 10			Injection volume : 30 μL n = 10			Injection volume : 500 μL n = 10		
Ion	Concentration	RSD (%)		Concentration	RSD (%)		Concentration	RSD (%)	
	mg/L	Retention time	Peak area	μg/L	Retention time	Peak area	μg/L	Retention time	Peak area
F	1	0.08	0.23	8	0.12	4.0	1	0.08	1.1
Cl	1	0.07	0.27	8	0.07	6.4	1	0.06	9.1
NO2	5	0.09	0.18	40	0.08	3.6	5	0.09	1.9
Br	5	0.10	0.18	40	0.11	5.7	5	0.07	2.4
NO3	5	0.12	0.19	40	0.08	4.0	5	0.09	3.6
PO4	10	0.04	0.23	80	0.09	5.7	10	0.08	5.6
SO4	5	0.09	0.25	40	0.10	5.5	5	0.10	6.4

2-1-4. Applications on TSKgel SuperIC AZ

1) Tap water

Figure 7 shows a chromatogram of tap water analyzed under the standard separation conditions. Determination results are shown in **Table 4**. Even trace fluoride ions (microgram per liter levels) could be determined well.

A minute negative peak (Peak No. 2) could also be confirmed on the chromatogram (**Figure 8**) between the water dip and fluoride ions. When the eluate of this peak was processed and quantitatively analyzed by plasma emission spectrometry (ICP-AES), silicon was detected, indicating a silicate ion ($HSiO_3^-$) peak. Although the silicate ion peak was eluted as a negative peak, a good linear relationship between concentration and peak intensity was confirmed (calibration curve), indicating that silicate ions in aqueous solutions can also be analyzed.

2) Environmental samples

Figures 9 and **10** show chromatograms of river water and rain water as environmental sample applications.

In each case, good chromatograms were obtained; trace phosphate ions could be determined in the river water, and trace organic acids, etc., could be determined in the rain water.

3) Combustion absorption liquid (elemental analysis)

Using a standard sample used in halogen sulfur analysis (S-benzylthiuronium chloride), the absorption liquid treated by oxygen flask combustion was analyzed. **Figure 11** shows a chromatogram of the absorption liquid. Determination results revealed 17.44% chlorine (theoretical value, 17.49%) and 15.86% sulfur (theoretical value, 15.82%). The finding that results were very consistent with theoretical values confirms that this system is suitable for analyzing ions in combustion absorption liquid.

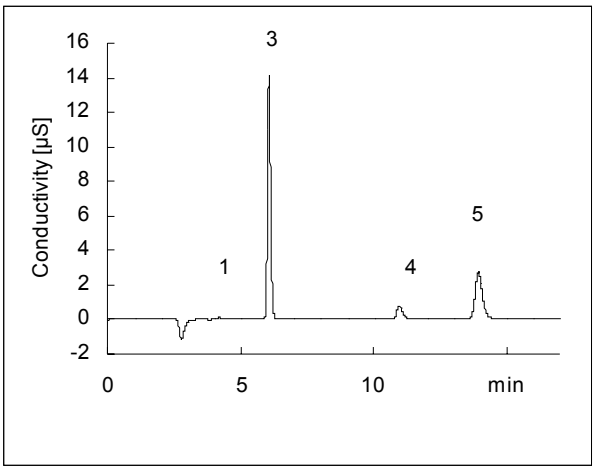

Figure 7 Analysis of tap water

Column:	TSKgel SuperIC-AZ (4.6 mm I.D. × 15 cm)	
Eluent:	1.9 mmol/L $NaHCO_3$ + 3.2 mmol/L Na_2CO_3	
Flow rate:	0.8 mL/min	
Detection:	Conductometric	
Temperature:	40 °C	
Suppressor gel:	TSKsuppressIC-A	
Samples:	1. F^- (0.044 mg/L)	2. $HSiO_3^-$ (5.621 mg/L)
	3. Cl^- (7.581 mg/L)	4. NO_3^- (1.661 mg/L)
	5. SO_4^{2-} (5.781 mg/L)	
Injection volume:	30 µL	

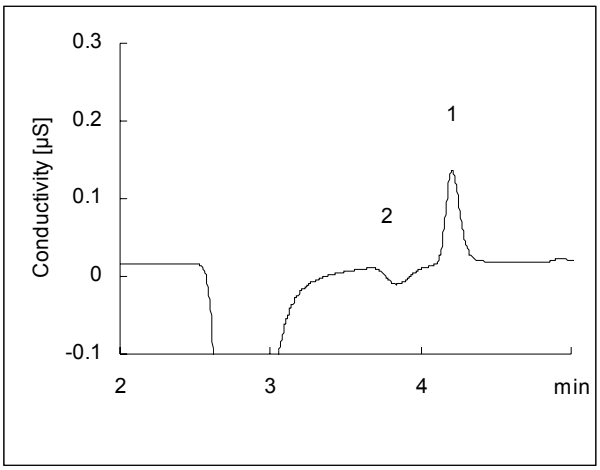

Figure 8 Analysis of tap water (enlargement of Figure 7)

Column:	TSKgel SuperIC-AZ (4.6 mm I.D. × 15 cm)	
Eluent:	1.9 mmol/L $NaHCO_3$ + 3.2 mmol/L Na_2CO_3	
Flow rate:	0.8 mL/min	
Detection:	Conductometric	
Temperature:	40 °C	
Suppressor gel:	TSKsuppressIC-A	
Samples:	1. F^- (0.044 mg/L)	2. $HSiO_3^-$ (5.621 mg/L)
	3. Cl^- (7.581 mg/L)	4. NO_3^- (1.661 mg/L)
	5. SO_4^{2-} (5.781 mg/L)	
Injection volume:	30 µL	

Table 4 Results of determination of anions in tap water

Tap water (n=15)		F^-	$HSiO_3^-$	Cl^-	NO_3^-	SO_4^{2-}
Concentration	(mg/L)	0.044	5.62	7.58	1.66	5.78
Retention time	RSD (%)	0.13	0.13	0.14	0.20	0.09
Peak area	RSD (%)	1.53	1.47	0.16	0.19	0.17

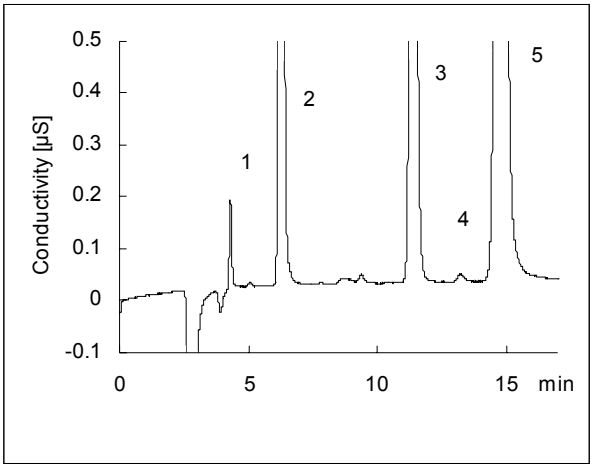

Figure 9 Analysis of river water

Column: TSKgel SuperIC-AZ (4.6 mm I.D. × 15 cm)
Eluent: 1.9 mmol/L $NaHCO_3$ + 3.2 mmol/L Na_2CO_3
Flow rate: 0.8 mL/min
Detection: Conductometric
Temperature: 40 °C
Suppressor gel: TSKsuppressIC-A
Samples: 1. F^- (0.057 μg/L) 2. Cl^- (6.85 μg/L)
3. NO_3^- (5.28 μg/L) 4. HPO_4^{2-} (0.071 μg/L)
5. SO_4^{2-} (11.56 μg/L)
Injection volume: 30 μL

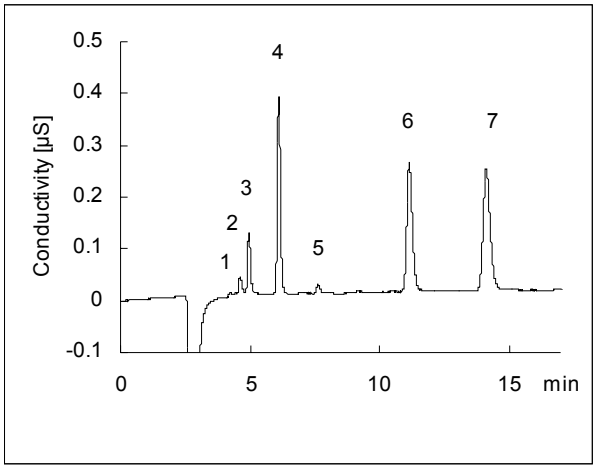

Figure 10 Analysis of rain water

Column: TSKgel SuperIC-AZ (4.6 mm I.D. × 15 cm)
Eluent: 1.9 mmol/L $NaHCO_3$ + 3.2 mmol/L Na_2CO_3
Flow rate: 0.8 mL/min
Detection: Conductometric
Temperature: 40 °C
Suppressor gel: TSKsuppressIC-A
Samples: 1. F^- (0.002 mg/L) 2. $CH_3CO_2^-$ (0.16 mg/L)
3. HCO_2^- (0.12 mg/L) 4. Cl^- (0.25 mg/L)
5. NO_2^- (0.02 mg/L) 6. NO_3^- (0.51 mg/L)
7. SO_4^{2-} (0.46 mg/L)
Injection volume: 30 μL

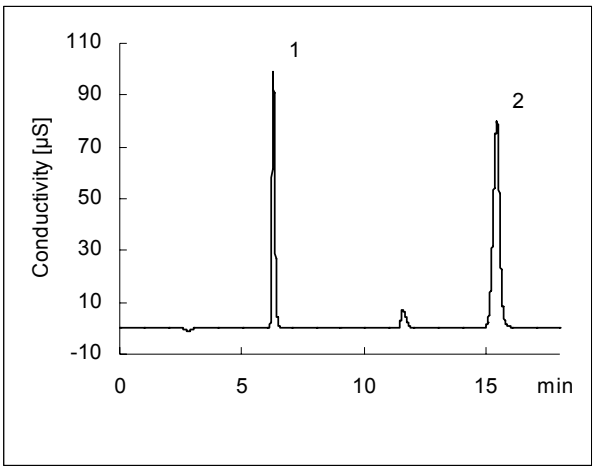

Figure 11 Analysis of anion in combustion absorption liquid

Column: TSKgel SuperIC-AZ (4.6 mm I.D. × 15 cm)
Eluent: 1.9 mmol/L $NaHCO_3$ + 3.2 mmol/L Na_2CO_3
Flow rate: 0.8 mL/min
Detection: Conductometric
Temperature: 40 °C
Suppressor gel: TSKsuppressIC-A
Samples: 1. Cl^- (40.41 mg/L) 2. SO_4^{2-} (110.07 mg/L)
Injection volume: 30 μL
Pretreatment of samples

Sample: S-Benzylthiuronium chloride (23.050 mg)
Combustion method: Oxygen flask combustion
Absorption liquid: 10 mL (10mmol/L NaOH + 0.6%H_2O_2)
Absorption liquid was diluted up to 100 mL

2-2. TSKgel SuperIC-Anion

The TSKgel SuperIC-Anion is a column used for anion analysis using the suppressor method with a borate buffer. The packing material comprises a styrene polymer gel (particle size: 5 µm) to which a quaternary ammonium group has been introduced. With the objective of high-speed high-resolution analysis primarily of 7 standard anions, analysis can be accomplished in approximately 12 min. Use of a borate buffer suppresses the water dip effect, and the ability to determine fast-eluting fluoride ions is better than with a carbonate buffer.

2-2-1. Chromatogram of standard anions

Table 5 shows the compositions of representative eluents.

1) Standard separation conditions

Figure 12 shows a chromatogram of 7 standard anions on TSKgel SuperIC-Anion. As a borate buffer is used in the eluent, conductivity is lower than with a carbonate buffer after suppression of the eluent itself. As a result, the water dip is decreased and baseline separation of fast-eluting fluoride ions becomes possible. Furthermore, since UV transmittance is higher than with a carbonate buffer, the ions with UV absorbance (3 species) can be detected with a high sensitivity. **Figure 13** shows a chromatogram with UV detection (wavelength: 210 nm) of 7 standard anions. When conductometric detection is used in combination with UV detection, in consideration of the pressure resistance of cell, the system is connected in the following order: column (suppressor); UV detector; and conductometric detector.

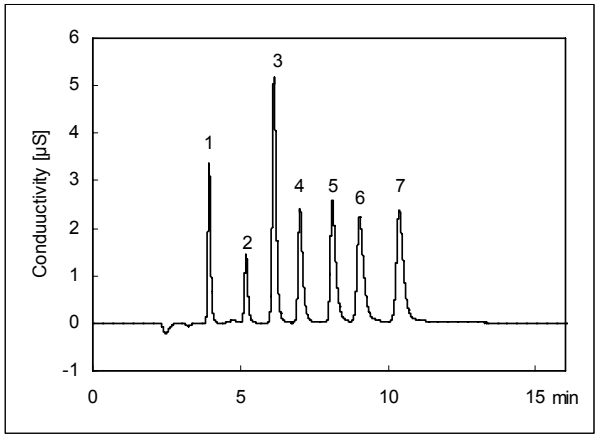

Figure 12 Separation of standard anions (conductometric detection)

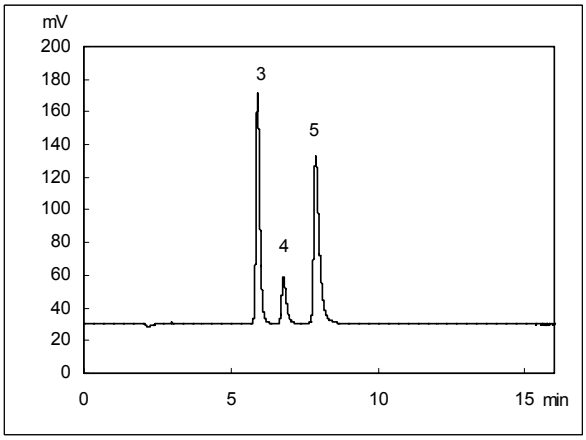

Figure 13 Separation of standard anions (UV detection)

Column: TSKgel SuperIC-Anion (4.6 mm I.D. × 15 cm)
Eluent: 6.0 mmol/L $Na_2B_4O_7$ + 15 mmol/L H_3BO_3 + 0.2 mol/L $NaHCO_3$
Flow rate: 0.8 mL/min
Detection: Conductometric
Temperature: 40 °C
Suppressor gel: TSKsuppressIC-A
Samples: 1. F^- (1 mg/L) 2. Cl^- (1 mg/L)
3. NO_2^- (5 mg/L) 4. Br^- (5 mg/L)
5. SO_3^- (5 mg/L) 6. HPO_4^{2-} (10 mg/L)
7. SO_4^{2-} (5 mg/L)
Injection volume: 30 µL

Detection: UV 210 nm; other conditions the same as in Figure 12.

Table 5 List of separation conditions (TSKgel SuperIC-Anion)

Eluent:	6.0 mmol/L $Na_2B_4O_7$ + 15 mmol/L H_3BO_3 + 0.2 mol/L $NaHCO_3$
Flow rate:	0.8 mL/min
Detection:	Conductometric
Temperature:	40 °C
Injection volume:	30 µL
Suppressor gel:	TSKsuppressIC-A

2-3.TSKgel SuperIC-AP

TSKgel SuperIC-AP uses a packing material comprising a hydrophilic polymer gel (particle size: 6 µm) to which a quaternary ammonium group has been introduced. This column can be used for anion analysis using the suppressor method with a carbonate buffer, as well as for anion analysis using the non-suppressor method with a gluconate buffer. The column is provided in two different lengths, 15 cm and 7.5 cm, which can be selected according to the components of the analyte and analysis time.

2-3-1. Chromatograms of standard anions

1) Standard separation conditions (suppressor method)

Figures 14 and **15** show chromatograms of 7 standard anions on TSKgel SuperIC-AP columns with 15- and 7.5-cm, respectively. The 15-cm column is used for samples requiring high resolution containing numerous impurities. The 7.5-cm column is used with samples in which the components are relatively pure.

2) Standard separation conditions (non-suppressor method)

In addition to the suppressor method in which a carbonate buffer is used, the TSKgel SuperIC-AP can also be used for anion analysis using a non-suppressor method with a gluconate buffer. **Figures 16** and **17** show chromatograms of 7 standard anions. Running costs can be reduced by using the non-suppressor method when analyte concentrations are high (when high-sensitivity analysis is unnecessary).

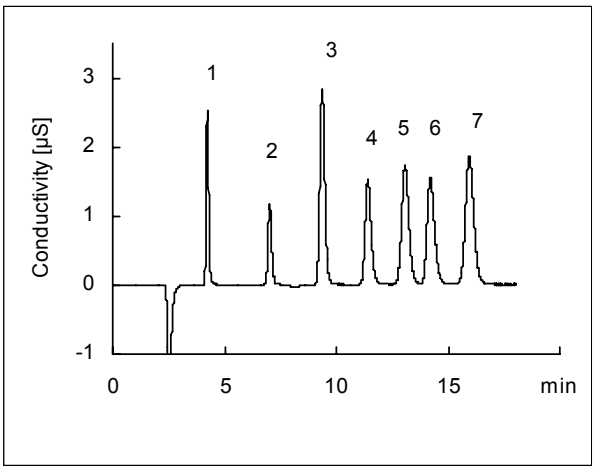

Figure 14 Separation of standard anions (standard separation conditions: suppressor method)

Column:	TSKgel SuperIC-AP (4.6 mm I.D. × 15 cm)	
Eluent:	2.9 mmol/L $NaHCO_3$ + 3.1 mmol/L Na_2CO_3	
Flow rate:	0.8 mL/min	
Detection:	Conductometric	
Temperature:	40 °C	
Suppressor gel:	TSKsuppressIC-A	
Samples:	1. F^- (1 mg/L)	2. Cl^- (1 mg/L)
	3. NO_2^- (5 mg/L)	4. Br^- (5 mg/L)
	5. SO_3^- (5 mg/L)	6. HPO_4^{2-} (10 mg/L)
	7. SO_4^{2-} (5 mg/L)	
Injection volume:	30 µL	

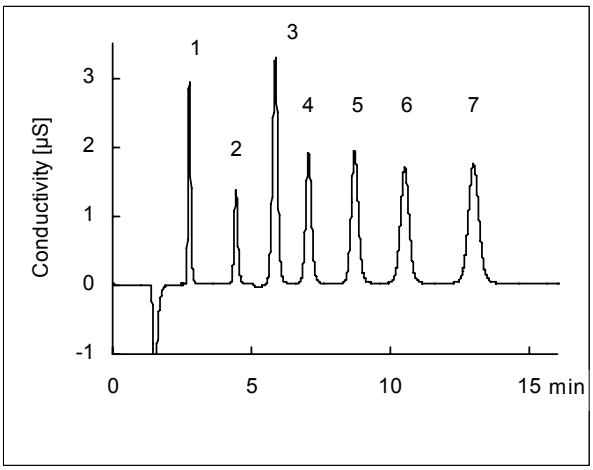

Figure 15 Separation of standard anions (Rapid separation conditions: suppressor method)

Column:	TSKgel SuperIC-AP (4.6 mm I.D. × 7.5 cm)	
Eluent:	3.4 mmol/L $NaHCO_3$ + 1.7 mmol/L Na_2CO_3	
Flow rate:	0.8 mL/min	
Detection:	Conductometric	
Temperature:	40 °C	
Suppressor gel:	TSKsuppressIC-A	
Samples:	1. F^- (1 mg/L)	2. Cl^- (1 mg/L)
	3. NO_2^- (5 mg/L)	4. Br^- (5 mg/L)
	5. SO_3^- (5 mg/L)	6. HPO_4^{2-} (10 mg/L)
	7. SO_4^{2-} (5 mg/L)	
Injection volume:	30 µL	

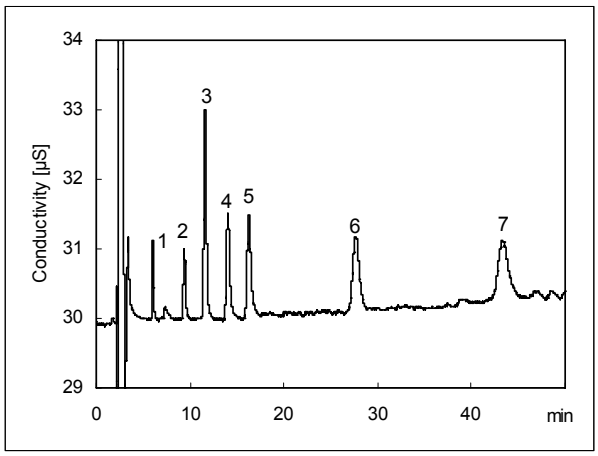

Figure 16 Separation of standard anions (Non-suppressor method: CM detection)

Column:	TSKgel SuperIC-AP (4.6 mm I.D. × 15 cm)	
Eluent:	1.3 mmol/L potassium gluconate + 1.3 mmol/L borax + 30 mmol/L boric acid + 10% acetonitrile + 0.5% glycerin	
Flow rate:	1.0 mL/min	
Detection:	Conductometric	
Temperature:	40 °C	
Suppressor gel:	TSKsuppressIC-A	
Samples:	1. F^- (1 mg/L)	2. Cl^- (1 mg/L)
	3. NO_2^- (5 mg/L)	4. Br^- (5 mg/L)
	5. SO_3^- (5 mg/L)	6. HPO_4^{2-} (10 mg/L)
	7. SO_4^{2-} (5 mg/L)	
Injection volume:	30 μL	

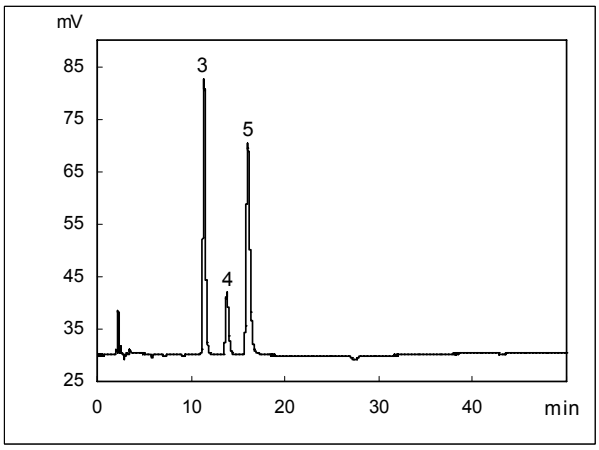

Figure 17 Separation of standard anions (Non-suppressor method: UV detection)

Detection: UV 210 nm
Other conditions are the same as in Figure 16.

3. Columns for Cation Analysis

3-1.TSKgel SuperIC-CR

TSKgel SuperIC-CR uses a packing material comprising a styrene gel (particle size: 3 µm) to which a carboxyl group has been introduced. This column can be used for cation analysis using the suppressor method with a methanesulfonic acid as eluent. The column is particularly good for separating Na ions and NH_4 ions, and is capable of measuring trace NH_4 ions in the presence of excessive Na ions.

3-1-1. Separation of standard cations

Figure 18 shows a chromatogram of 6 standard cations on TSKgel SuperIC-CR. An eluent containing 18-crown-6 ether is used to improve the separation of Na and NH_4 ions. Crown ether delays the elution of NH_4 and K ions, and K ions are eluted after Ca ions. Histidine is added with the objective of improving the peak shape of bivalent cations.

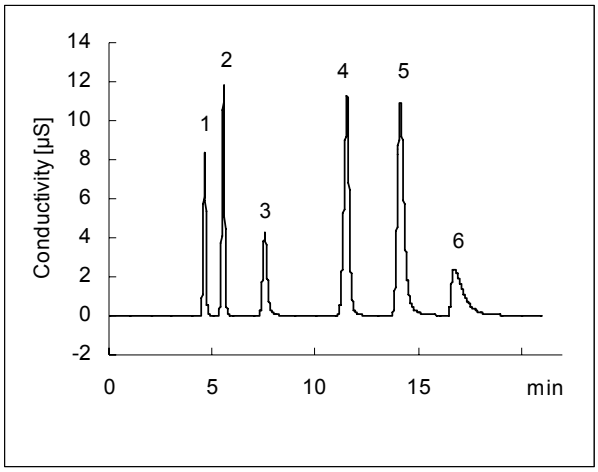

Figure 18 Separation of standard cations (Standard separation conditions: suppressor method)

Column:TSKgel SuperIC-CR (4.6 mm I.D. × 15 cm)
Eluent: 2.2 mmol/L methanesulfonic acid + 1.0 mmol/L 18-crown-6 ether + 0.5 mmol/L histidine
Flow rate: 0.7 mL/min
Detection: Conductometric
Temperature: 40 °C
Suppressor gel: TSKsuppressIC-C
Samples: 1. Li^+ (1 mg/L) 2. Na^+ (5 mg/L)
3. NH_4^+ (5 mg/L) 4. Mg^{2+} (5 mg/L)
5. Ca^{2+} (10 mg/L) 6. K^+ (10 mg/L)
Injection volume: 30 µL

3-1-2. Flow rate dependence

Figure 19 shows the relationship between flow rate and height equivalent to a theoretical plate for Na ions under standard separation conditions. TSKgel SuperIC-CR shows the highest column efficiency at flow rates of 0.4-0.7 mL/min. However, in consideration of analysis time, a flow rate of 0.7 mL/min is recommended.

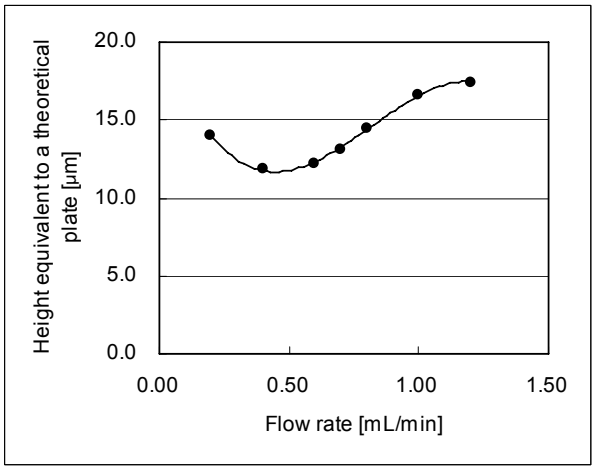

Figure 19 Flow rate dependence of column efficiency

Column: TSKgel SuperIC-CR (4.6 mm I.D. × 15 cm)
Eluent: 2.2 mmol/L methanesulfonic acid + 1.0 mmol/L 18-crown-6 ether + 0.5 mmol/L histidine
Flow rate: 0.2-1.2 mL/min
Detection: Conductometric
Temperature: 40 °C
Suppressor gel: TSKsuppressIC-C
Samples: Na^+ (5 mg/L)
Injection volume: 30 µL

3-1-3. Analysis of trace NH_4 ions

1) Determination of NH_4 ions in the presence of Na ions (30 mg/L)

Figure 20 compares chromatograms produced with and without Na ions (30 mg/L); **Figure 21** shows the calibration curve and plot. As NH_4 ions are well separated to Na ions, the peak shape of NH_4 is normal and the good calibration curves from low to the high concentration ranges are obtained

2) Analysis repeatability

The repeatability of analysis of NH_4 ions (ammoniacal nitrogen: 0.02 mg/L in the form of NH_4-H) was investigated, and the chromatogram is shown in **Figure 22**. Peak area RSD was 3.0%, clearly demonstrating that trace NH_4 ions can be determined with good repeatability.

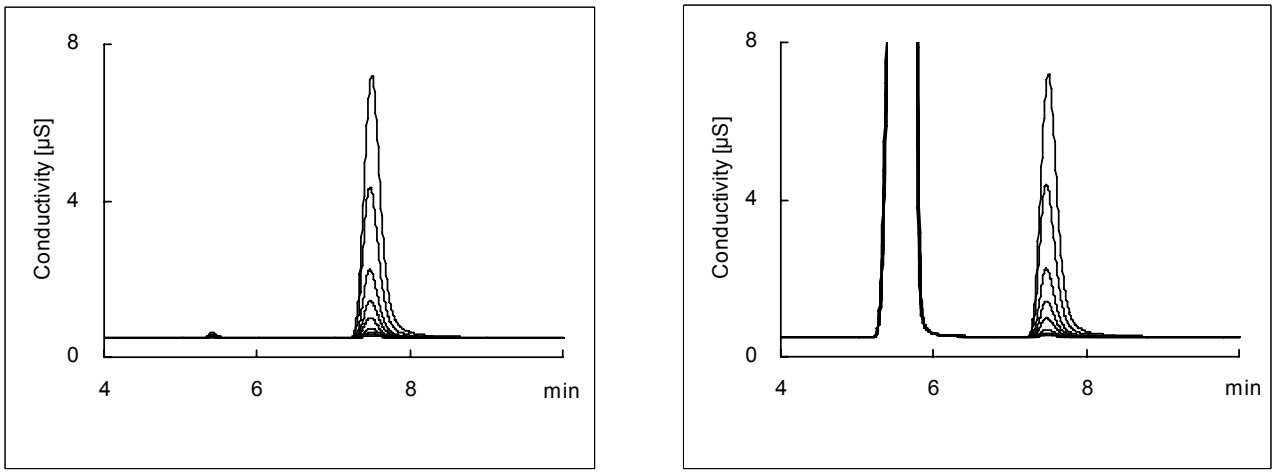

Figure 20 Separation of NH_4 ions in the presence of a high concentration of Na ions
Left: Without Na ions
Right: In the presence of 30 mg/L Na ions

Column:	TSKgel SuperIC-CR (4.6 mm I.D. × 15 cm)
Eluent:	2.2 mmol/L methanesulfonic acid + 1.0 mmol/L 18-crown-6 ether + 0.5 mmol/L histidine
Flow rate:	0.7 mL/min
Detection:	Conductometric
Temperature:	40 °C
Suppressor gel:	TSKsuppressIC-C
Samples:	NH_4^+ (0.03 to 10.0 mg/L)
Injection volume:	30 µL

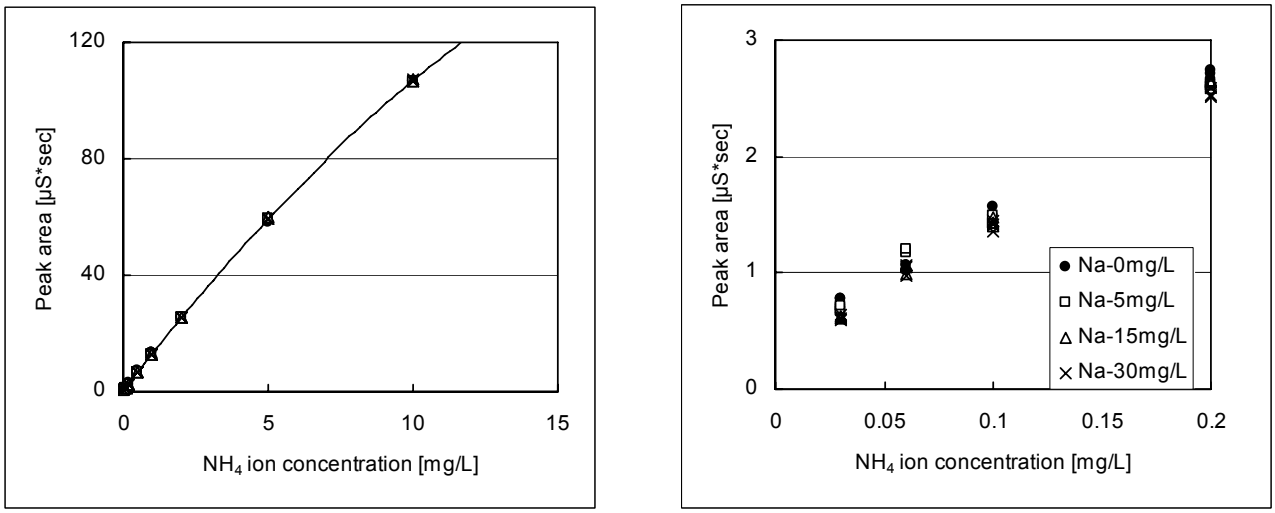

Figure 21 Calibration curve and plot of NH_4 ions in the presence of a high concentration of Na ions
Left: High concentration range (0.03-10 mg/L)
Right: Low concentration range (0.03-0.2 mg/L)

Column: TSKgel SuperIC-CR (4.6 mm I.D. × 15 cm)
Eluent: 2.2 mmol/L methanesulfonic acid + 1.0 mmol/L 18-crown-6 ether + 0.5 mmol/L histidine
Flow rate: 0.7 mL/min
Detection: Conductometric
Temperature: 40°C
Suppressor gel: TSKsuppressIC-C
System: IC-2001
Samples: NH_4^+ (0.03 to 10.0 mg/L)
Injection volume: 30 µL

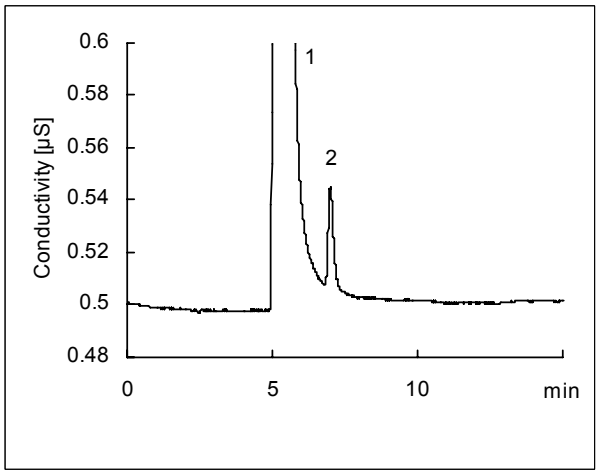

Figure 22 Separation of NH_4 ions in the presence of high concentration of Na ions (Standard separation conditions: Suppressor method)

Column: TSKgel SuperIC-CR (4.6 mm I.D. × 15 cm)
Eluent: 2.2 mmol/L methanesulfonic acid + 1.0 mmol/L 18-crown-6 ether + 0.5 mmol/L histidine
Flow rate: 0.7 mL/min
Detection: Conductometric
Temperature: 40 °C
Suppressor gel: TSKsuppressIC-C
Samples: 1. Na^+ (30 mg/L)
2. NH_4^+ (0.02 mg/L in the form of NH_4-H)
Injection volume: 30 µL
*Analysis repeatability (Peak area of NH_4 ions)
RSD (n = 8): 3.0%

3-1-4. Applications on TSKgel SuperIC-CR

Figures 23 to **25** show chromatograms of tap water, river water and sea water as real samples.

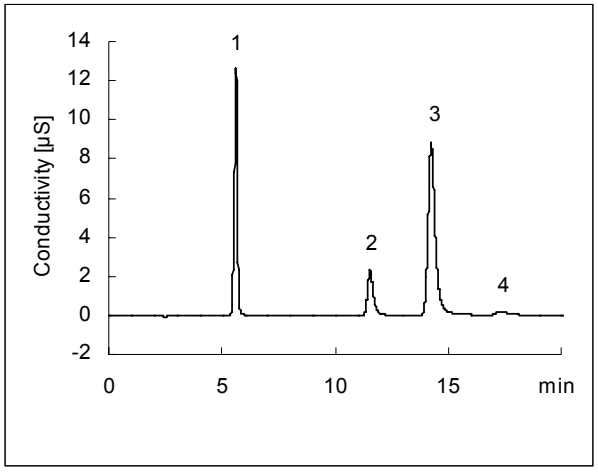

Figure 23 Analysis of tap water (Standard separation conditions: Suppressor method)

Column:TSKgel SuperIC-CR (4.6 mm I.D. × 15 cm)
Eluent: 2.2 mmol/L methanesulfonic acid + 1.0 mmol/L 18-crown-6 ether + 0.5 mmol/L histidine
Flow rate: 0.7 mL/min
Detection: Conductometric
Temperature: 40 °C
Suppressor gel: TSKsuppressIC-C
Samples: 1. Na^+ (67 mg/L) 2. K^+ (0.8 mg/L) 3. Mg^{2+} (1.1 mg/L) 4. Ca^{2+} (9.6 mg/L)
Injection volume: 30 µL

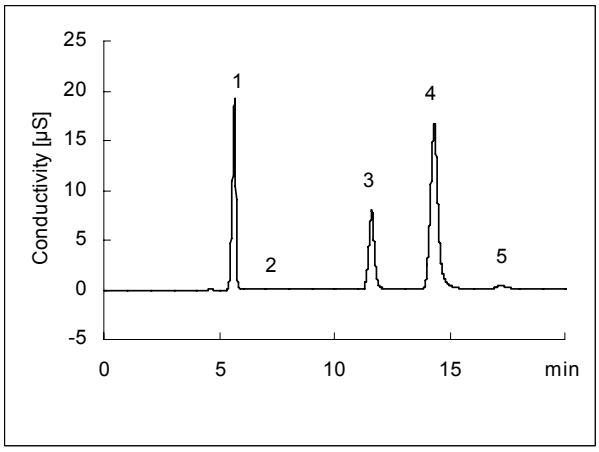

Figure 24 Analysis of river water (Standard separation conditions: Suppressor method)

Column: TSKgel SuperIC-CR (4.6 mm I.D. × 15 cm)
Eluent: 2.2 mmol/L methanesulfonic acid + 1.0 mmol/L 18-crown-6 ether + 0.5 mmol/L histidine
Flow rate: 0.7 mL/min
Detection: Conductometric
Temperature: 40 °C
Suppressor gel: TSKsuppressIC-C
Samples: 1. Na^+ (11.7 mg/L) 2. NH_4^+ (0.007 mg/L) 3. Mg^{2+} (3.7 mg/L) 4. Ca^{2+} (18.9 mg/L) 5. K^+ (1.6 mg/L)
Injection volume: 30 µL

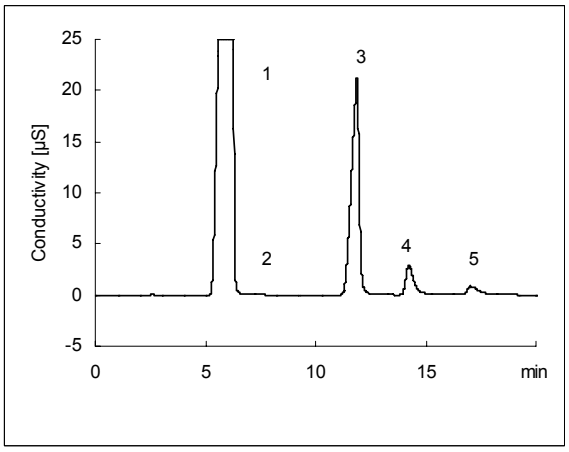

Figure 25 Analysis of sea water (Standard separation conditions: Suppressor method)

Column:TSKgel SuperIC-CR (4.6 mm I.D. × 15 cm)
Eluent: 2.2 mmol/L methanesulfonic acid + 1.0 mmol/L 18-crown-6 ether + 0.5 mmol/L histidine
Flow rate: 0.7 mL/min
Detection: Conductometric
Temperature: 40 °C
Suppressor gel: TSKsuppressIC-C
Samples: 1. Na^+ (11.7 mg/L) 2. NH_4^+ (0.007 mg/L) 3. Mg^{2+} (3.7 mg/L) 4. Ca^{2+} (18.9 mg/L) 5. K^+ (1.6 mg/L)
Injection volume: 30 µL
* Injected after diluting 100-fold with ion exchange water.

4. Columns for simultaneous analysis of anion/cation

4-1. TSKgel SuperIC-A/C

TSKgel SuperIC-A/C is an analytical column unique to Tosoh, which uses both an ion exclusion mode and an ion exchange mode to allow simultaneous analysis of anions and cations. The packing material comprises a hydrophilic polymer gel (particle size: 4 μm) to which a carboxyl group has been introduced.

4-1-1. Separation of standard ions

Figure 26 shows a chromatogram of standard anions and cations on TSKgel SuperIC-A/C. With this column, first the anions then the cations are eluted. Analysis time for the 9 standard ion species is approximately 20 minutes. Positive and negative peaks between the anions and cations eluted at around 5 min are peaks derived from the eluent and the sample matrix (system peaks).

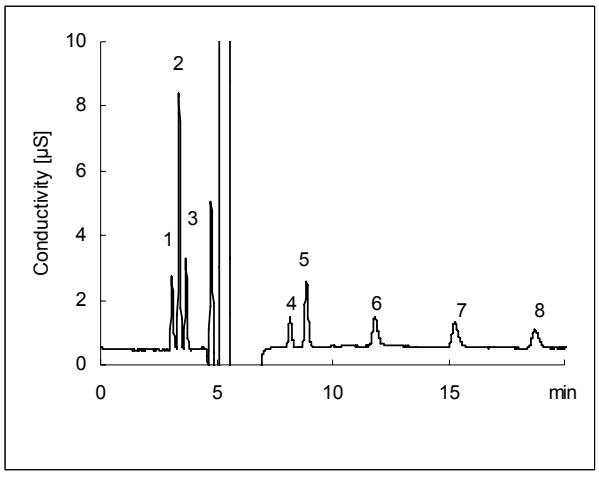

Figure 26 Separation of standard ions

Column:	TSKgel SuperIC-A/C (6.0 mm I.D. × 15 cm)	
Eluent:	6.0 mmol/L 18-crown-6 ether + 0.45 mmol/L 5-sulfosalicylic acid + 5.0 mmol/L L-tartaric acid + 5% (v/v) acetonitrile	
Flow rate:	0.6 mL/min	
Detection:	Conductometric	
Temperature:	40 °C	
Samples:	1. SO_4^{2-} (1.6 mg/L)	2. Cl^- (2.95 mg/L)
	3. NO_3^- (2.07 mg/L)	4. Na^+ (0.38 mg/L)
	5. NH_4^+ (0.90 mg/L)	6. K^+ (1.3 mg/L)
	7. Mg^{2+} (0.41 mg/L)	8. Ca^{2+} (0.67 mg/L)
Injection volume:	30 μL	

4-1-2. Effects of eluent composition

The standard separation conditions use an eluent composed of tartaric acid, sulfosalicylic acid, 18-crown-6 ether and acetonitrile. Effects of the concentrations of sulfosalicylic acid and crown ether on the separation of the standard ions were investigated.

1) Effect of sulfosalicylic acid

Figure 27 shows retention time of ions at the different concentration of suflosalicylic acid in eluent with standard condition.

For the cations (left), due to the ion exchange mode, retention time decreases for each ion as the acid concentration increases. However, for the anions (right), if the acid concentration increases, the ion exclusion effect decreases, permeation into the gel occurs more readily, so resolution for each ion is improved. In consideration of the balance between anionic and cationic separation, the sulfosalicylic acid concentration was optimized at 0.45 mmol/L for standard conditions.

Although a similar effect is seen with tartaric acid, due to differences in the degree to which cation/anion separation is influenced by the concentrations added, a mixed system of both acids is used for the standard conditions.

2) Effect of crown ether concentration

Figure 28 shows retention time of ions at the different concentration of 18-crown-6 ether in eluent with standard condition. In the case of 18-crown-6 ether, because the chelating effect is most apparent on K ions, the retention time for K ions is markedly delayed as the concentration increases. This also contributes to a slight increase in separation of NH_4 and K ions. In consideration of the balance between anionic and cationic separation, the 18-crown-6 ether concentration was optimized at 6.0 mmol/L for standard conditions.

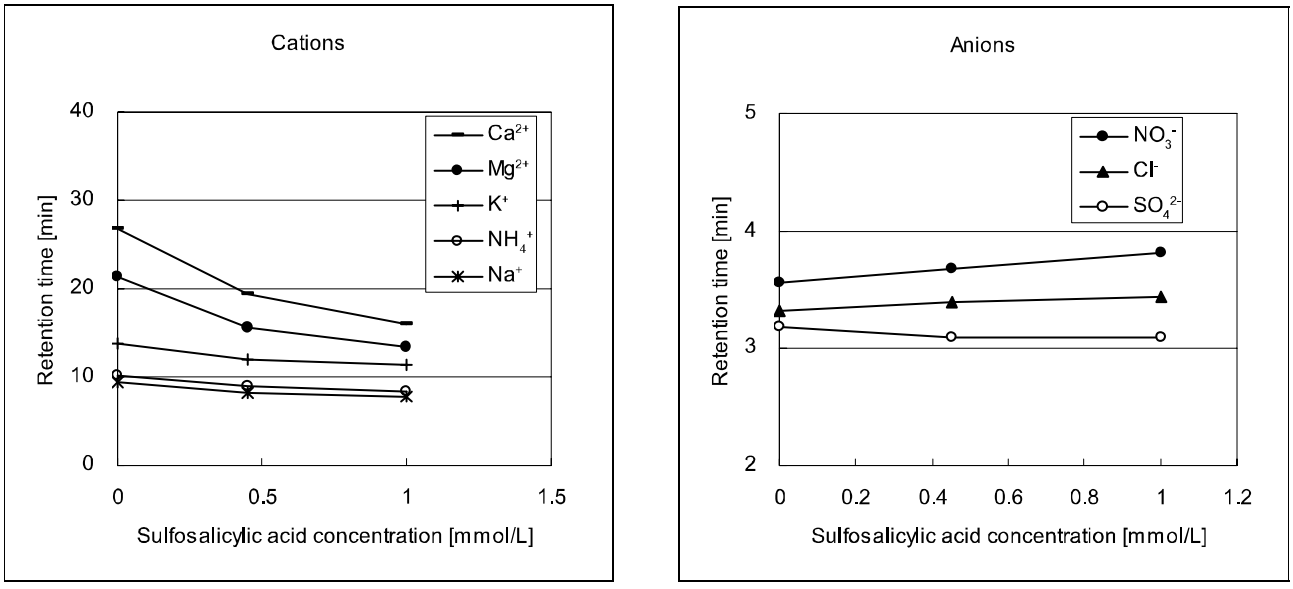

Figure 27 Effect of concentration of sulfosalicylic acid in eluent on retention time

Column:	TSKgel SuperIC-A/C (6.0 mm I.D. × 15 cm)			
Eluent:	6.0 mmol/L 18-crown-6 ether + 0 to 1.0 mmol/L 5-sulfosalicylic acid + 5.0 mmol/L L-tartaric acid + 5% (v/v) acetonitrile			
Flow rate:	0.6 mL/min			
Detection:	Conductometric			
Temperature:	40 °C			
Samples:	1. SO_4^{2-} (1.6 mg/L)	2. Cl^- (2.95 mg/L)	3. NO_3^- (2.07 mg/L)	4. Na^+ (0.38 mg/L)
	5. NH_4^+ (0.90 mg/L)	6. K^+ (1.3 mg/L)	7. Mg^{2+} (0.41 mg/L)	8. Ca^{2+} (0.67 mg/L)
Injection volume:	30 µL			

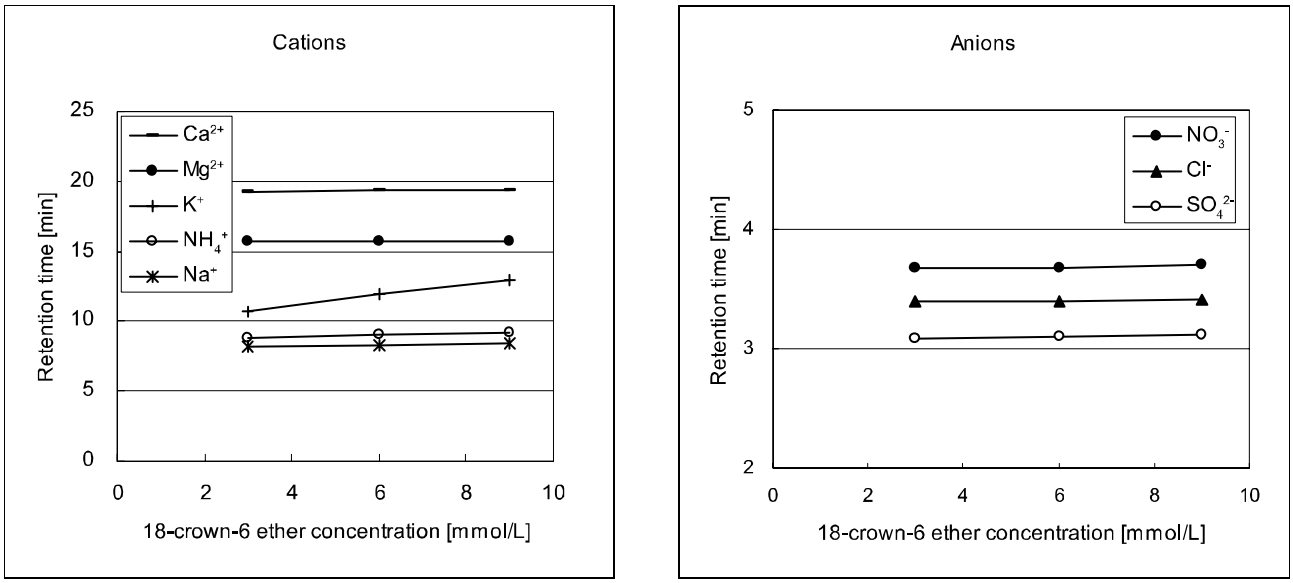

Figure 28 Effect of concentration of crown ether in eluent on retention time

Column: TSKgel SuperIC-A/C (6.0 mm I.D. × 15 cm)
Eluent: 1.0-9.0 mmol/L 18-crown-6 ether + 0.45 mmol/L 5-sulfosalicylic acid + 5.0 mmol/L L-tartaric acid + 5% (v/v) acetonitrile
Flow rate: 0.6 mL/min
Detection: Conductometric
Temperature: 40 °C
Samples: 1. SO_4^{2-} (1.6 mg/L) 2. Cl^- (2.95 mg/L) 3. NO_3^- (2.07 mg/L) 4. Na^+ (0.38 mg/L)
5. NH_4^+ (0.90 mg/L) 6. K^+ (1.3 mg/L) 7. Mg^{2+} (0.41 mg/L) 8. Ca^{2+} (0.67 mg/L)
Injection volume: 30 µL

4-1-3. Applications on TSKgel SuperIC-A/C

1) Application to rain water analysis

In monitoring environmental water such as acid rain, etc., it is useful to analyze the ions contained and calculate the ion balance to understand the history of the issue. **Figure 29** shows a chromatogram of rain water; and **Table 6** shows the results of analysis of ion balance. Using this column, the information required for analyzing ion balance can be obtained with one ion analysis run and a measurement of the pH.

2) Applications to samples with a high concentration of matrix

A characteristic of this column is that nonionic substances are eluted between anions and cations. Utilizing this characteristic, ions can be analyzed from samples containing high concentrations of non-ionic substances. **Figure 30** shows chromatogram of analyzing ions in acetic acid. Normally, when measured with a column used for anion analysis, the giant acetic acid ion peak would impede results (**Figure 31**). However, with this column, good anion analysis is possible because acetic acid is eluted in the system peak region. **Figure 32** shows chromatogram of analysis of an infusion solution. Although this sample contains large quantities of sugars, ions are well detected. **Figure 33** shows chromatogram of analysis of a bath additive. Analysis was performed after removing highly hydrophobic components by solid-phase extraction using the TOYOPAK ODS. Although the sample contains large quantities of carbonic acid, both carbonic acid and carbonate ions are eluted in the system peak region, enabling good determination of the ions.

Table 6 Ion balance of rain water

Ionic species	Concentration (μ eq/L)
SO_4^{2-}	44.6
Cl^-	24.5
NO_3^-	9.19
Na^+	9.13
NH_4^+	22.2
Ca^{2+}	32.4
H^+	(pH 4.85)
Total anions	78.3
Total cations	77.9
Ion balance	1.01

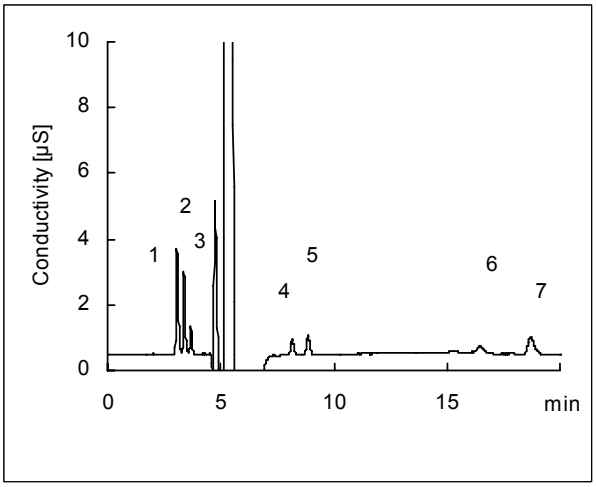

Figure 29 Analysis of rain water

Column: TSKgel SuperIC-A/C (6.0 mm I.D. × 15 cm)
Eluent: 6.0 mmol/L 18-crown-6 ether + 0.45 mmol/L 5-sulfosalicylic acid + 5.0 mmol/L L-tartaric acid + 5% (v/v) acetonitrile
Flow rate: 0.6 mL/min
Detection: Conductometric
Temperature: 40 °C
Samples: 1. SO_4^{2-} 2. Cl^- 3. NO_3^- 4. Na^+ 5. NH_4^+ 6. Unknown 7. Ca^{2+}
Injection volume: 30 μL

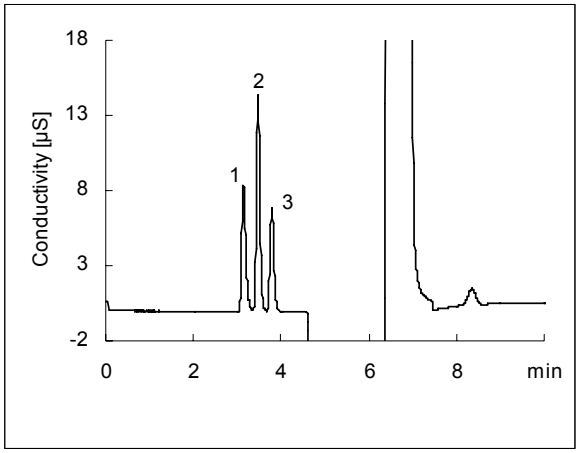

Figure 30 Analysis of acetic acid

Column:TSKgel SuperIC-A/C (6.0 mm I.D. × 15 cm)
Eluent: 6.0 mmol/L 18-crown-6 ether + 0.45 mmol/L 5-sulfosalicylic acid + 5.0 mmol/L L-tartaric acid + 5% (v/v) acetonitrile
Flow rate: 0.6 mL/min
Detection: Conductometric
Temperature: 40 °C
Samples: 1. SO_4^{2-} (5 mg/L) 2. Cl^- (5 mg/L) 3. NO_3^- (5 mg/L)
Injection volume: 30 μL

* Analyzed after adding standard anions to acetic acid (special grade reagent, 10%)

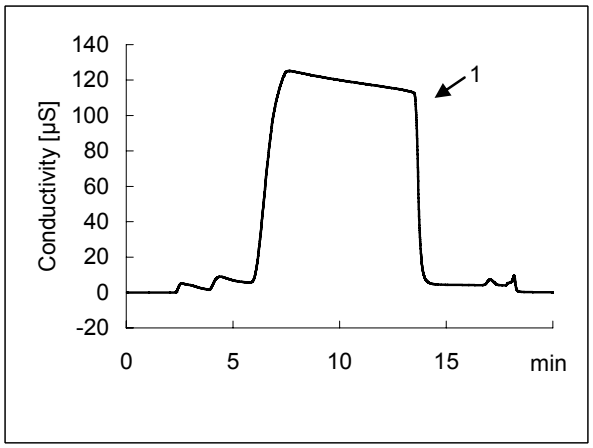

Figure 31 Analysis of acetic acid (TSKgel SuperIC-AP standard separation conditions: suppressor method)

Column: TSKgel SuperIC-AP (4.6 mm I.D. × 15 cm)
Eluent: 2.9 mmol/L $NaHCO_3$ + 3.1 mmol/L Na_2CO_3
Flow rate: 0.8 mL/min
Detection: Conductometric
Temperature: 40 °C
Suppressor gel: TSKsuppressIC-A
Samples: 1. Acetic acid (special grade reagent 10%)
Injection volume: 30 μL

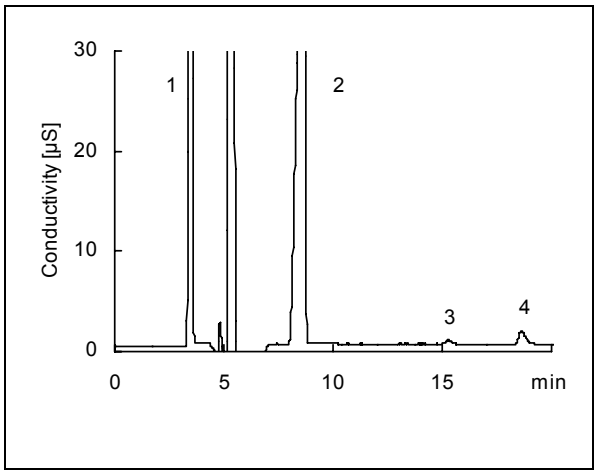

Figure 32 Analysis of infusion solution

Column: TSKgel SuperIC-A/C (6.0 mm I.D. × 15 cm)
Eluent: 6.0 mmol/L 18-crown-6 ether + 0.45 mmol/L 5-sulfosalicylic acid + 5.0 mmol/L L-tartaric acid + 5% (v/v) acetonitrile
Flow rate: 0.6 mL/min
Detection: Conductometric
Temperature: 40 °C
Samples: 1. Cl^- (74.6 mg/L) 2. Na^+ (60.9 mg/L) 3. Mg^{2+} (0.24 mg/L) 4. Ca^{2+} (1.58 mg/L)
Injection volume: 30 μL

* Infusion solution analyzed after diluting 50-fold.

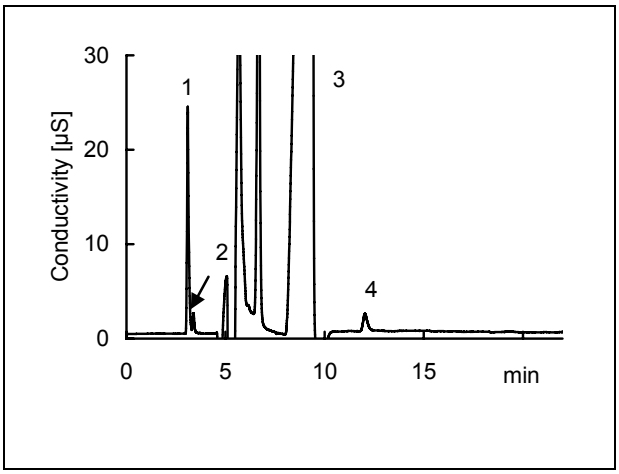

Figure 33 Analysis of bath additive

Column: TSKgel SuperIC-A/C (6.0 mm I.D. × 15 cm)
Eluent: 6.0 mmol/L 18-crown-6 ether + 0.45 mmol/L 5-sulfosalicylic acid + 5.0 mmol/L L-tartaric acid + 5% (v/v) acetonitrile
Flow rate: 0.6 mL/min
Detection: Conductometric
Temperature: 40 °C
Samples: 1. SO_4^{2-} (10.5 mg/L) 2. Cl^- (0.75 mg/L) 3. Na^+ (undetermined) 4. K^+ (2.65 mg/L)

Injection volume: 30 μL
* Pretreatment: 0.1% aqueous solution treated with TOYOPAK ODS

5. Conclusion

A variety of packed columns have been assembled in the TSKgel SuperIC columns for high-performance IC. We believe that by selecting the optimum packed column in accordance with the sample characteristics and the analysis objectives, the field of application for IC will be increasingly improved and expanded.