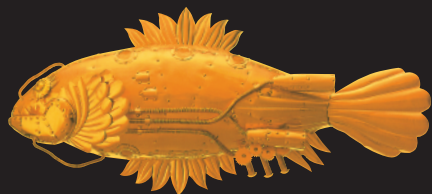


Shodex™



HPLC Columns

Shodex™ Ion Chromatography columns

Anion and cation analysis with suppressor and non-suppressor methods

**Technical notebook
No. 8**



**SHOWA
DENKO**
EUROPE

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1. Lineup of Shodex Ion Chromatography Columns

Shodex offers a wide range of columns for ion analysis. Choose a column best suited to your separation needs and equipment.

1-1. Column selection

● Anion Analysis [Suppressor method]	IC SI-90 4E	Inorganic anions (standard column)
	IC SI-50 4E	Inorganic anions and organic acids
	IC SI-52 4E	Inorganic anions and oxyhalides Inorganic anions and organic acids
	IC SI-35 4D	Inorganic anions and oxyhalides (rapid analysis)
	IC SI-91 4C	Oxyhalides (post-column method)
	WINE VH-anion 4D	Sulfite ion in wine
	[Non-suppressor method]	IC NI-424
	IC I-524A	Inorganic anions (standard column)
● Cation Analysis	IC YS-50	Higher performance type of YK-421 Transition metals With suppressor and non-suppressor method
	ICYK-421	Monovalent and divalent cations Alkylamines
	ICY-521	Monovalent or divalent cations

1-2. Specifications

● Anion analysis

[Suppressor method]

Product Code	Product Name	Functional Group	Base Material	Plate Number (TP/column)	Particle Size (µm)	Column Size (mm) I.D. x L
F6995244 F6709620	IC SI-90 4E IC SI-90G	Quaternary ammonium	Polyvinyl alcohol	> 5,000 guard column	9 9	4.0 x 250 4.6 x 10
F6995245 F6709625	IC SI-50 4E IC SI-50G	Quaternary ammonium	Polyvinyl alcohol	> 10,000 guard column	5 5	4.0 x 250 4.6 x 10
F6995260 F6709626	IC SI-52 4E IC SI-92G	Quaternary ammonium	Polyvinyl alcohol	> 14,000 guard column	5 9	4.0 x 250 4.6 x 10
F6995290 F6709627	IC SI-35 4D IC SI-95G	Quaternary ammonium	Polyvinyl alcohol	> 13,000 guard column	3.5 9	4.0 x 150 4.6 x 10
F6995280 F6709620	IC SI-91 4C IC SI-90G	Quaternary ammonium	Polyvinyl alcohol	> 2,500 guard column	9 9	4.0 x 100 4.6 x 10
F6995263 F6709623	WINE VH-anion 4D WINE VH-anionG 4A	Quaternary ammonium	Polyvinyl alcohol	> 7,000 guard column	5 9	4.0 x 150 4.6 x 10

[Non-suppressor method]

Product Code	Product Name	Functional Group	Base Material	Plate Number (TP/column)	Particle Size (µm)	Column Size (mm) I.D. x L
F6995243 F6709616	IC NI-424 IC NI-G	Quaternary ammonium	Polyhydroxymethacrylate	> 5,000 guard column	5 5	4.6 x 100 4.6 x 10
F6995240 F6700400	IC I-524A IC IA-G	Quaternary ammonium	Polyhydroxymethacrylate	> 2,000 guard column	12 12	4.6 x 100 4.6 x 10

● Cation analysis

Product Code	Product Name	Functional Group	Base Material	Plate Number (TP/column)	Particle Size (µm)	Column Size (mm) I.D. x L
F7122000 F6700530	IC YS-50 IC YS-G	Carboxyl	Polyvinyl alcohol	> 5,500 guard column	5 5	4.6 x 125 4.6 x 10
F7122012 F6709608	IC YK-421 IC YK-G	Carboxyl	Silica	> 2,800 guard column	5 5	4.6 x 125 4.6 x 10
F6995210 F6700230	IC Y-521 IC Y-G	Sulfo	Styrene divinylbenzene copolymer	> 3,000 guard column	12 12	4.0 x 150 4.6 x 10

2. Principles of Ion Chromatography

Ion chromatography, one form of liquid chromatography, separates and quantifies inorganic anions and cations, organic acids, organic bases, and a variety of other ions. Separation mechanisms including ion-exchange, ion-exclusion, and ion-pair chromatography are used. This technical notebook focuses on ion-exchange chromatography, in which ion exchange resin is used to separate counterions.

[Principles of Ion-Exchange Chromatography]

In ion-exchange chromatography, electrostatic interactions resulting from Coulomb forces are used to separate counterions on ion exchange resin. Using anion analysis as an example, below figure presents the principles of ion chromatography.

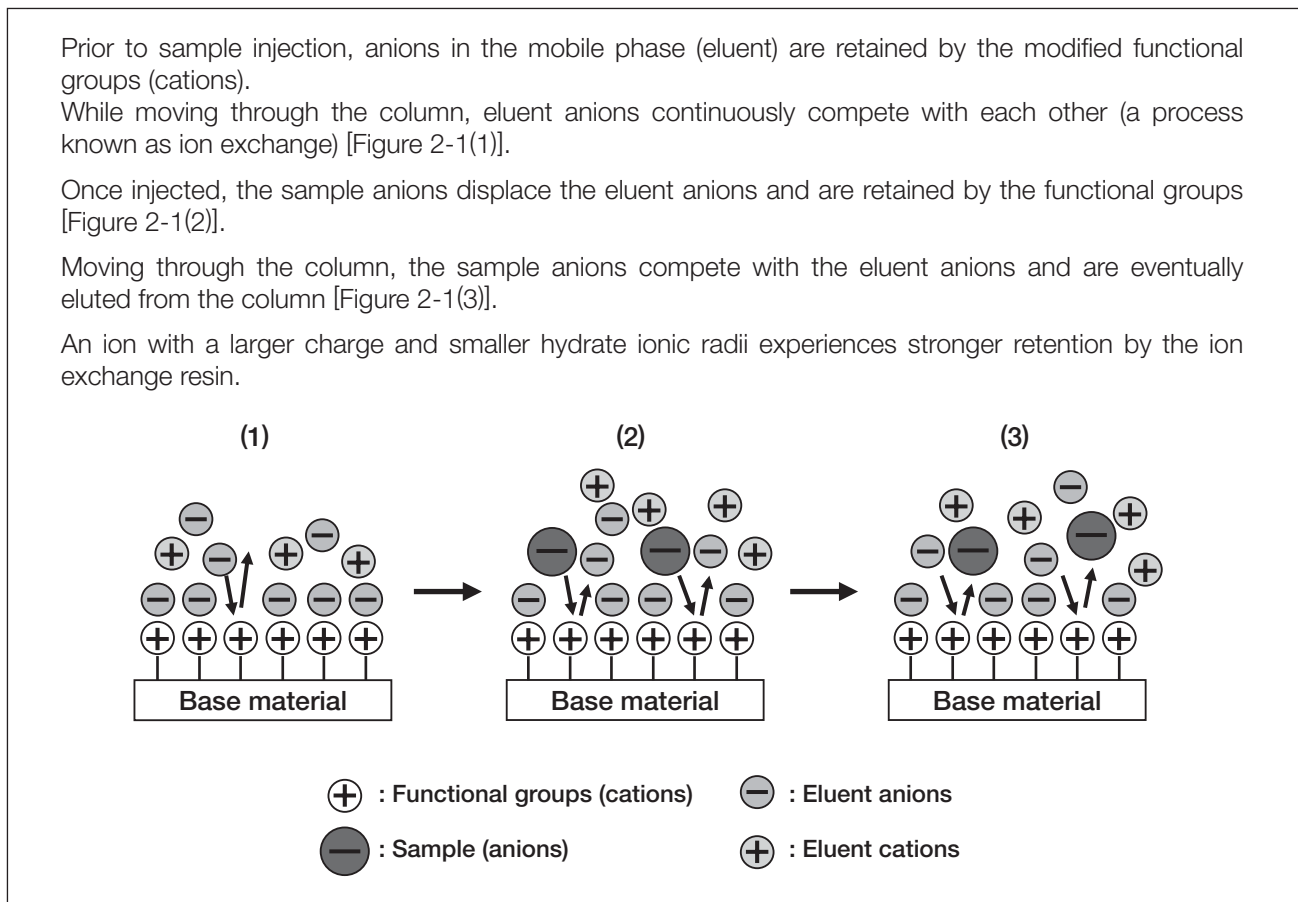


Fig.2-1 Separation mechanism of anion analysis

A conductivity detector is generally used for ion analysis because ions are excellent conductors. Current flows when a voltage is applied across two electrodes immersed in an ionic solution. Conductivity refers to the capacity of an electrolyte to conduct current. The concentration of ions can be determined by comparing the conductivity to that of a standard sample of known concentration of target ions. Ion chromatography employs an electrolytic solution as an eluent, which means that the eluent itself also exhibits conductivity. Eluent with high conductivity (i.e., background conductivity) results in high background noise and consequently decreases sensitivity. There are two methodologies of electrical conductivity detection. Suppressed conductivity method removes counter ions of the eluent after separation, thus reduces background noise. The other methodology, non-suppressed conductivity detection, uses a low-conductivity eluent instead.

[Suppressor Method]

Placing a device called a suppressor between the analytical column and the conductivity detector reduces the background conductivity. Suppressor method makes it possible to detect the analytes at low micrograms per litre range.

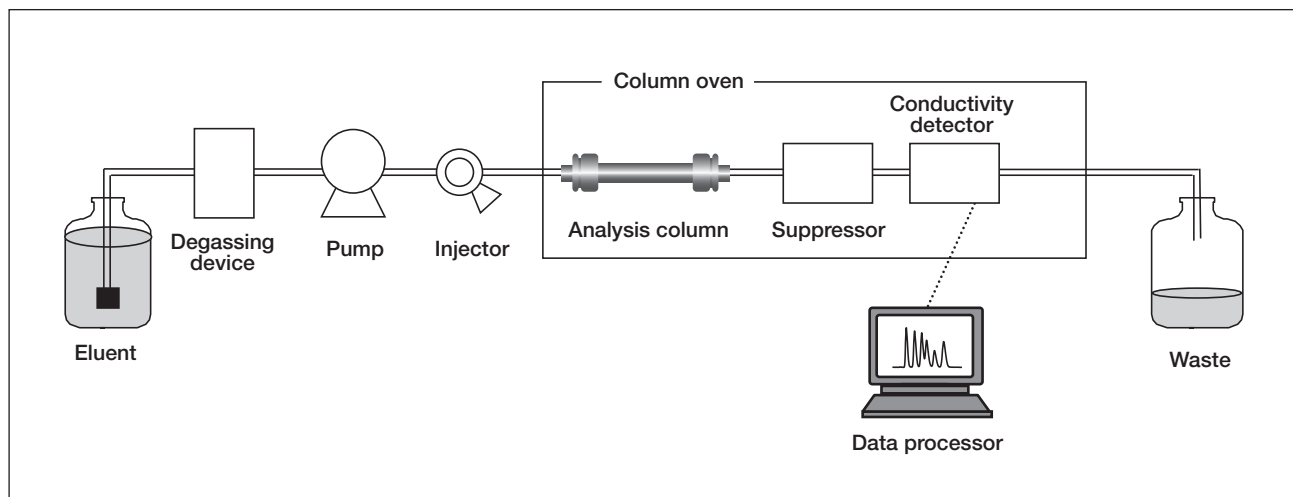


Fig.2-2 System configuration of suppressor method

[Non-suppressor Method]

The configuration of non-suppressor method (i.e., without suppressor) is simple and relatively less expensive than suppressor-method.

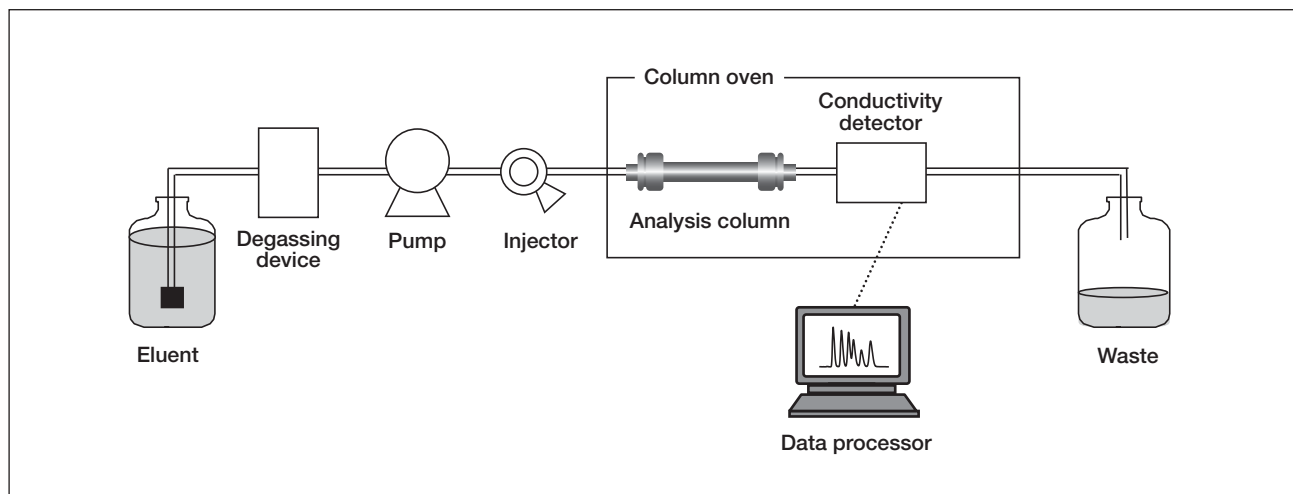


Fig.2-3 System configuration of non-suppressor method

Alternatively, ultraviolet/visible absorbance detectors, electrochemical detectors, mass spectrometers, and other detectors may be used depending on the target ions.

3. Anion analysis

3-1. Suppressor method

IC SI-90 4E is an analysis column for anion analysis with the suppressor method. It provides rapid and robust analysis of seven common anions by using an aqueous solution of 1.8mM sodium carbonate and 1.7mM sodium hydrogen carbonate as the eluent. At a flow rate of 1.5mL/min, sulfate ion elutes at approximately 10minutes. The IC SI-90 4E fulfills U.S. EPA Methods 300.0 (A) requirements.

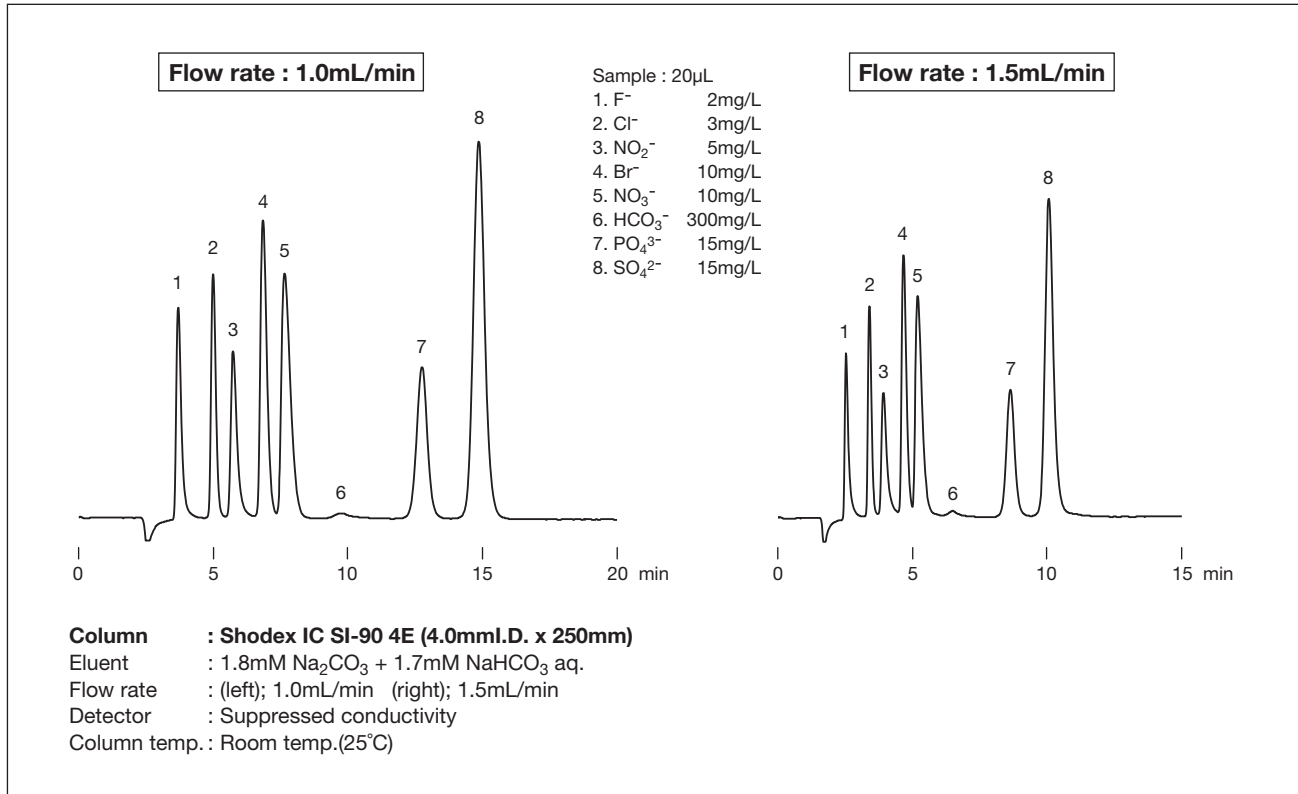


Fig. 3-1 Analysis of seven common anions

By optimizing the eluent conditions, IC SI-90 4E provides sensitive and improved separation of organic acids from inorganic anions.

Table 3-1. Retention time of anions

	(min)				(min)				(min)		
	(1)	(2)	(3)		(1)	(2)	(3)		(1)	(2)	(3)
F ⁻	3.5	3.9	4.7	NO ₂ ⁻	5.3	6.3	9.0	oxalic acid	14.6	20.6	30.7
acetic acid	3.7	4.2	5.1	Br ⁻	6.4	7.6	11.5	I ⁻	14.7	19.8	34.4
formic acid	4.0	4.5	5.6	ClO ₃ ⁻	6.3	7.8	12.0	WO ₄ ²⁻	17.6	25.1	38.2
ClO ₂ ⁻	4.2	4.8	6.3	NO ₃ ⁻	7.1	8.8	13.4	MoO ₄ ²⁻	19.0	27.1	42.0
methacrylic acid	4.3	4.9	6.4	PO ₄ ³⁻	11.3	15.0	14.1	S ₂ O ₃ ²⁻	18.5	26.4	42.5
BrO ₃ ⁻	4.4	5.1	6.7	SO ₃ ²⁻	12.7	18.2	27.5	CrO ₄ ²⁻	20.0	28.9	46.0
Cl ⁻	4.7	5.5	7.2	SO ₄ ²⁻	13.1	18.4	27.2	SCN ⁻	23.8	33.8	66.6

Column : Shodex IC SI-90 4E (4.0mmI.D. x 250mm)
Eluent : (1) 1.8mM Na₂CO₃ + 1.7mM NaHCO₃ aq.
 (2) 1.0mM Na₂CO₃ + 4.0mM NaHCO₃ aq.
 (3) 12mM NaHCO₃ aq.
Flow rate : 1.0mL/min
Detector : Suppressed conductivity
Column temp. : 25°C

Phosphate (HPO_4^{2-}), phosphite (HPO_3^{2-}), and hypophosphite (HPO_2^{2-}) ions were simultaneously analyzed with seven common anions. An aqueous solution of 12mM sodium hydrogen carbonate (NaHCO_3) as the eluent provided the strongest retention among the three eluents in Table 3-1. However, absorption of carbon dioxide into carbonate-based eluents causes a change in pH and consequently, retention times. The eluent should therefore be prepared at least once per day on an as-needed basis to ensure good reproducibility.

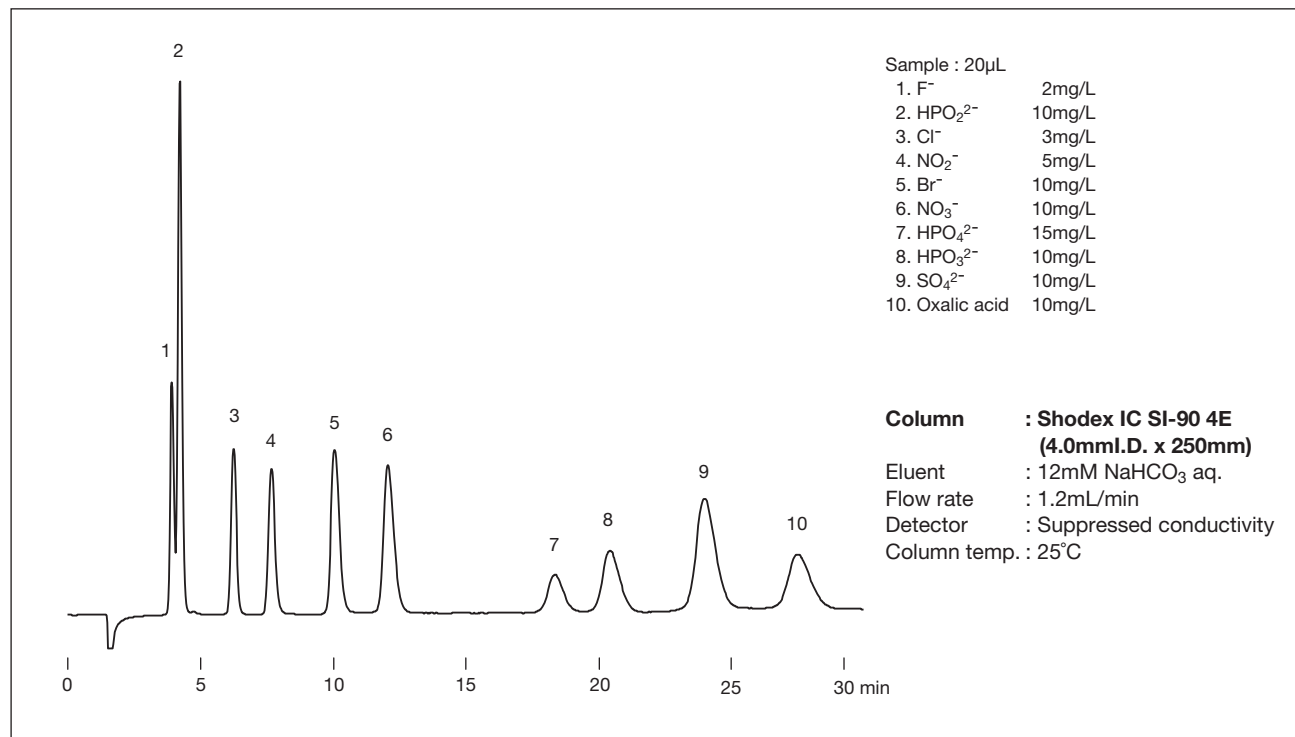


Fig.3-2 Phosphate, phosphite and hypophosphite ions

High-sensitivity analysis for seven common anions was conducted. An eluent containing 1mM sodium carbonate and 4mM sodium hydrogen carbonate is recommended for low-concentration analyte injection volume of more than 50 μL or samples with high carbonate concentrations.

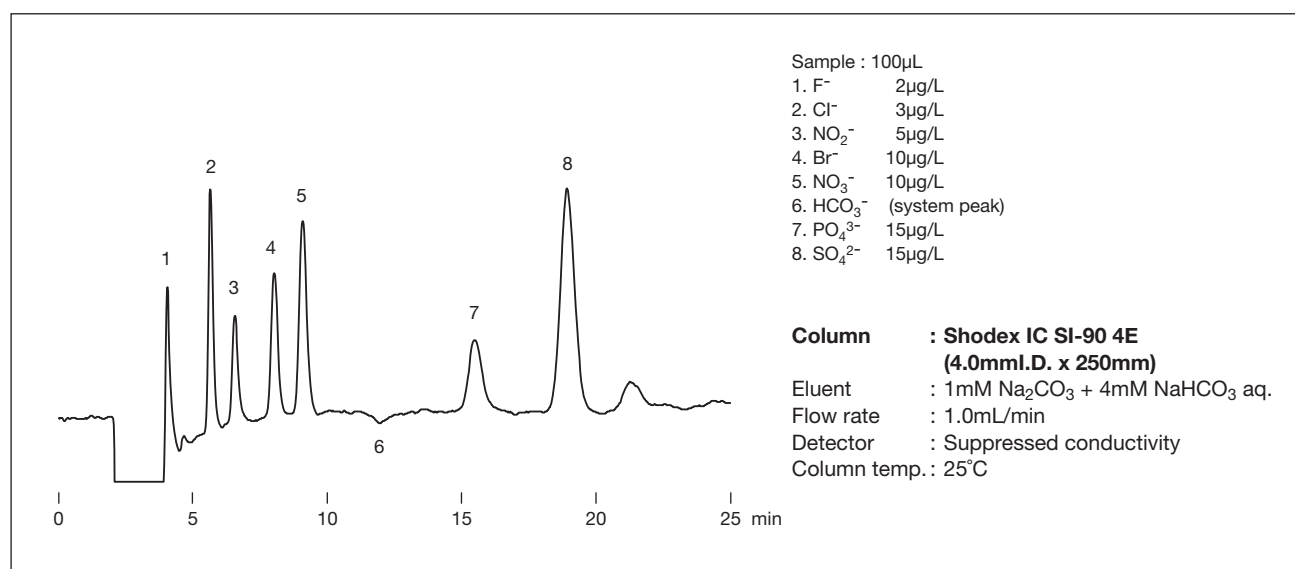


Fig. 3-3 High-sensitivity analysis using IC SI-90 4E

Conductivity detectors are not suitable for the reliable detection of hydrogen sulfide ion. A conductivity detector is connected in series with an ultraviolet absorption detector (UV) for the simultaneous separation and detection of following ions:

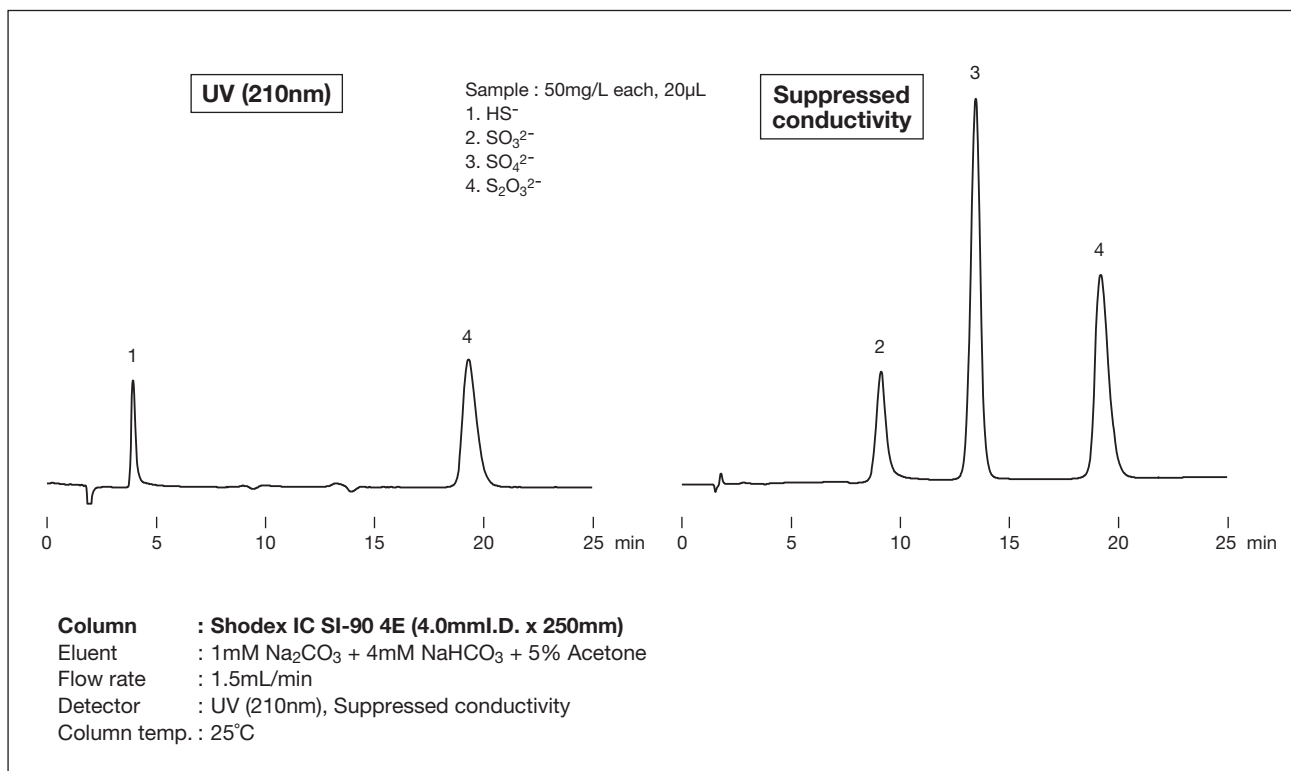


Fig. 3-4 Analysis of hydrogen sulfide, sulfite, sulfate and thiosulfate

IC SI-50 4E, an analytical column for anion analysis with the suppressor method, is used to analyze organic acids and anions simultaneously. IC SI-50 4E provides improved resolution compare to IC SI-90 4E; IC SI-50 4E completely separate acetic acid, formic acid, and methacrylic acid. The IC SI-50 4E fulfills U.S. EPA Methods 300.0 (A) requirements.

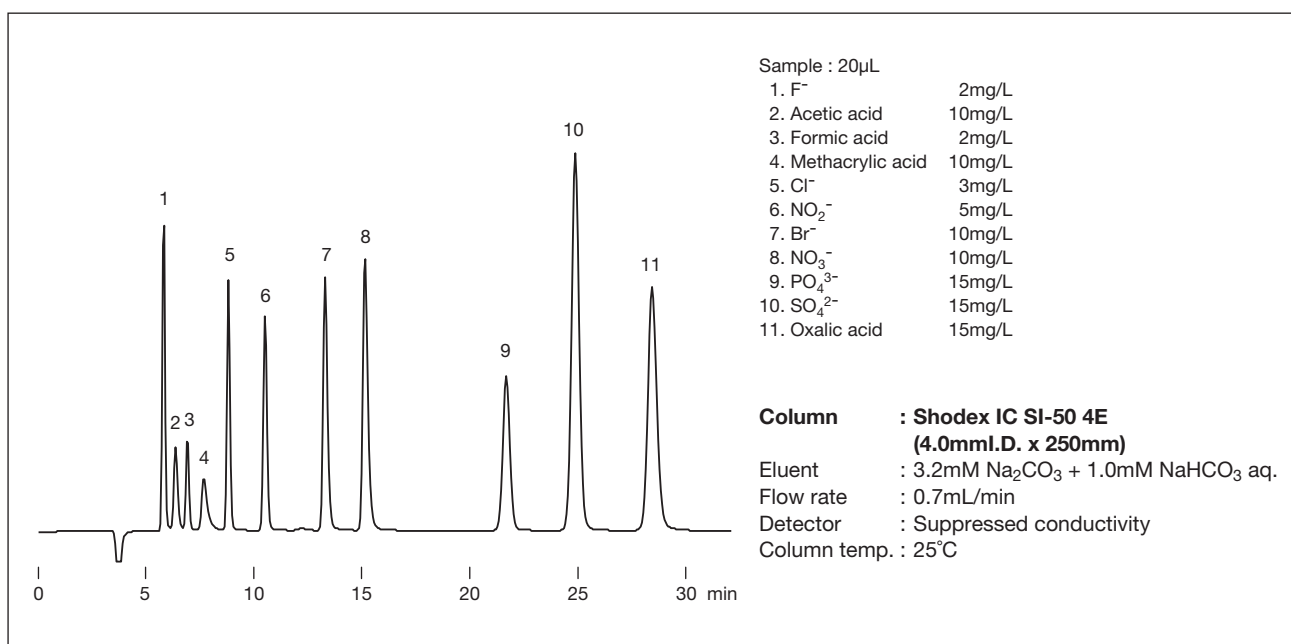


Fig. 3-5 Analysis of organic acids and seven common anions using IC SI-50 4E

IC SI-52 4E, an analytical column for anion analysis with the suppressor method, is suitable for the simultaneous analysis of oxyhalides and anions. IC SI-52 4E provides baseline separations of chlorite (ClO_2^-) and bromate (BrO_3^-) ions, and bromide (Br^-) and chlorate (ClO_3^-) ions which were not possible using IC SI-90 4E nor IC SI-50 4E. The IC SI-52 4E fulfills U.S. EPA Methods 300.0 (A) and (B) requirements.

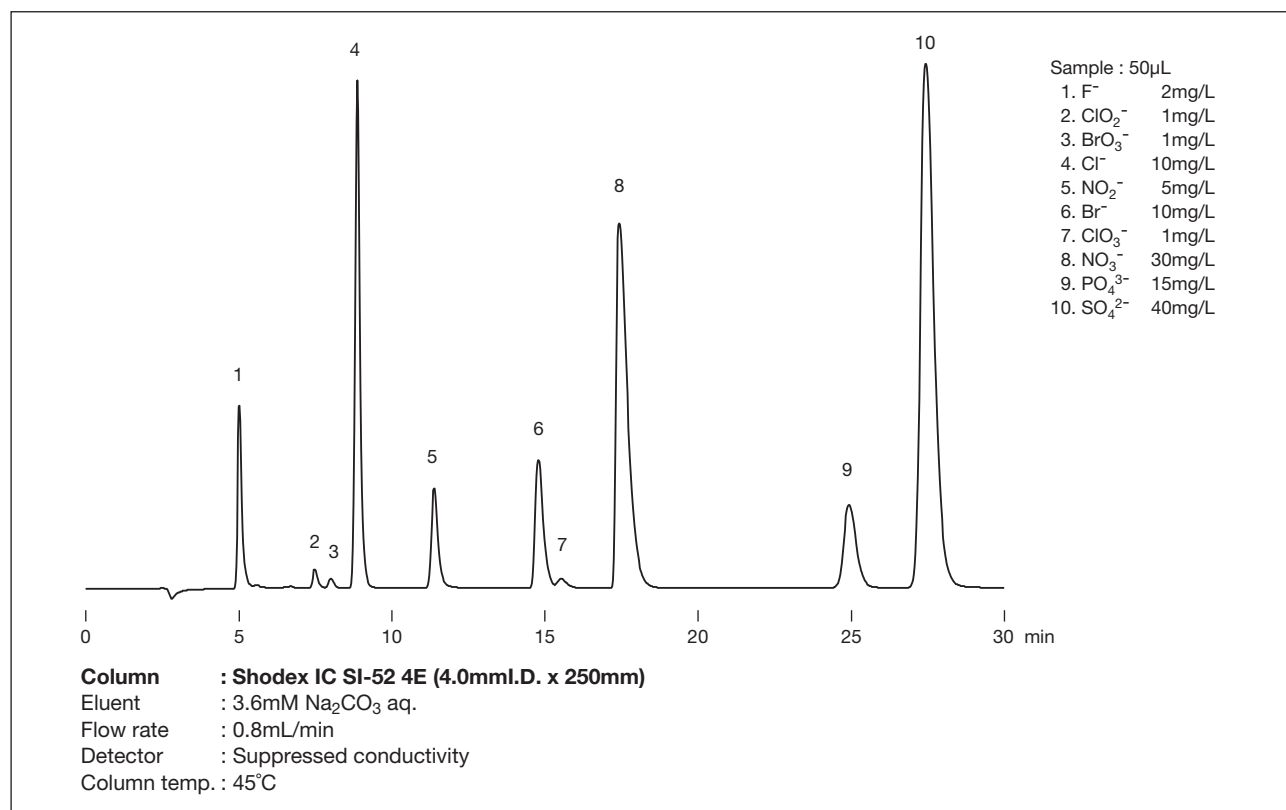


Fig. 3-6 Analysis of oxyhalides and seven common anions using IC SI-52 4E

The elution time of the ions are influenced by the column temperature. For the analysis of oxyhalides and anions using IC SI-52 4E, column temperature of 45°C is recommended to achieve separation of chlorate (ClO_3^-) from bromide (Br^-).

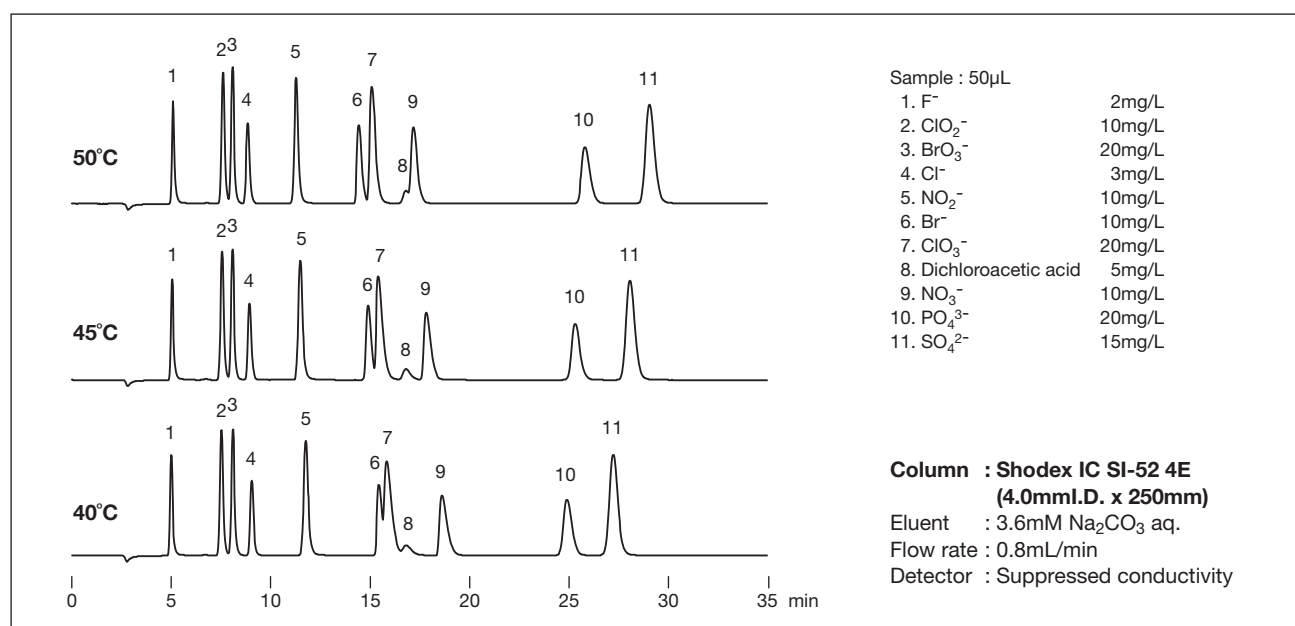


Fig. 3-7 Temperature-dependent properties of IC SI-52 4E

IC SI-35 4D provides rapid analysis of oxyhalides and inorganic anions; 50% faster than the IC SI-52 4E. This IC SI-35 4D fulfills U.S. EPA Methods 300.0 (A) and (B) requirements.

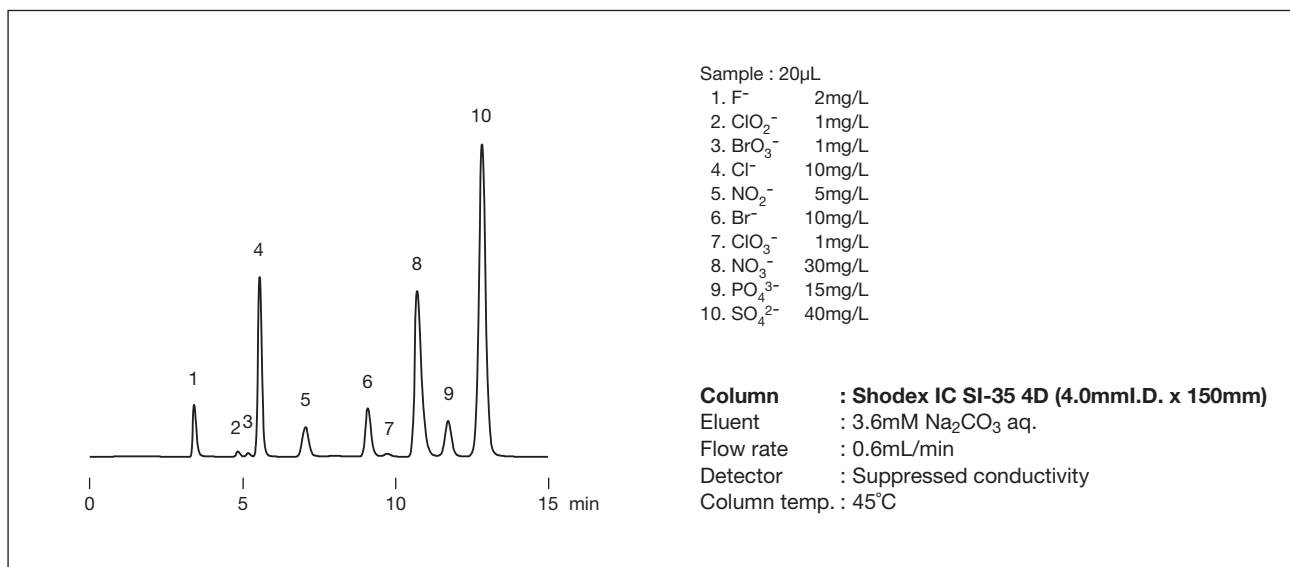


Fig. 3-8 Analysis of oxyhalides and seven common anions using IC SI-35 4D

Not only inorganic ions and oxyhalides, but IC SI-35 4D is suitable for the separation of organic acids. The long elution time (i.e., more than 30 minutes for succinic acid and malonic acid) required by IC SI-52 4E was shortened to 15 minutes using IC SI-35 4D.

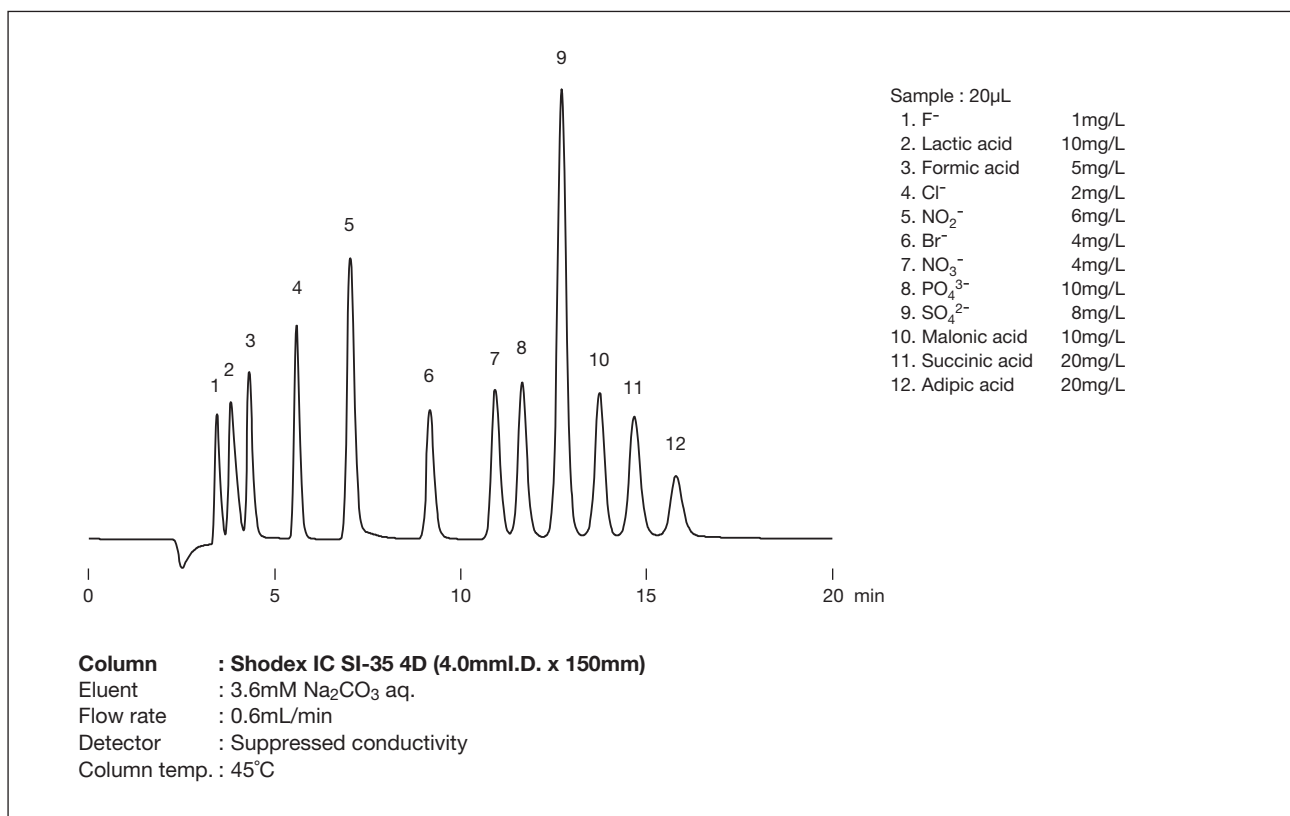


Fig. 3-9 Analysis of organic acids and common anions using IC SI-35 4D

3-2. Non-suppressor method

Seven common anions were analyzed by non-suppressor method. High-performance IC NI-424 has a theoretical plate number about twice that of IC I-524A. IC NI-424 separates phosphate and fluoride ions, which is difficult by IC I-524A.

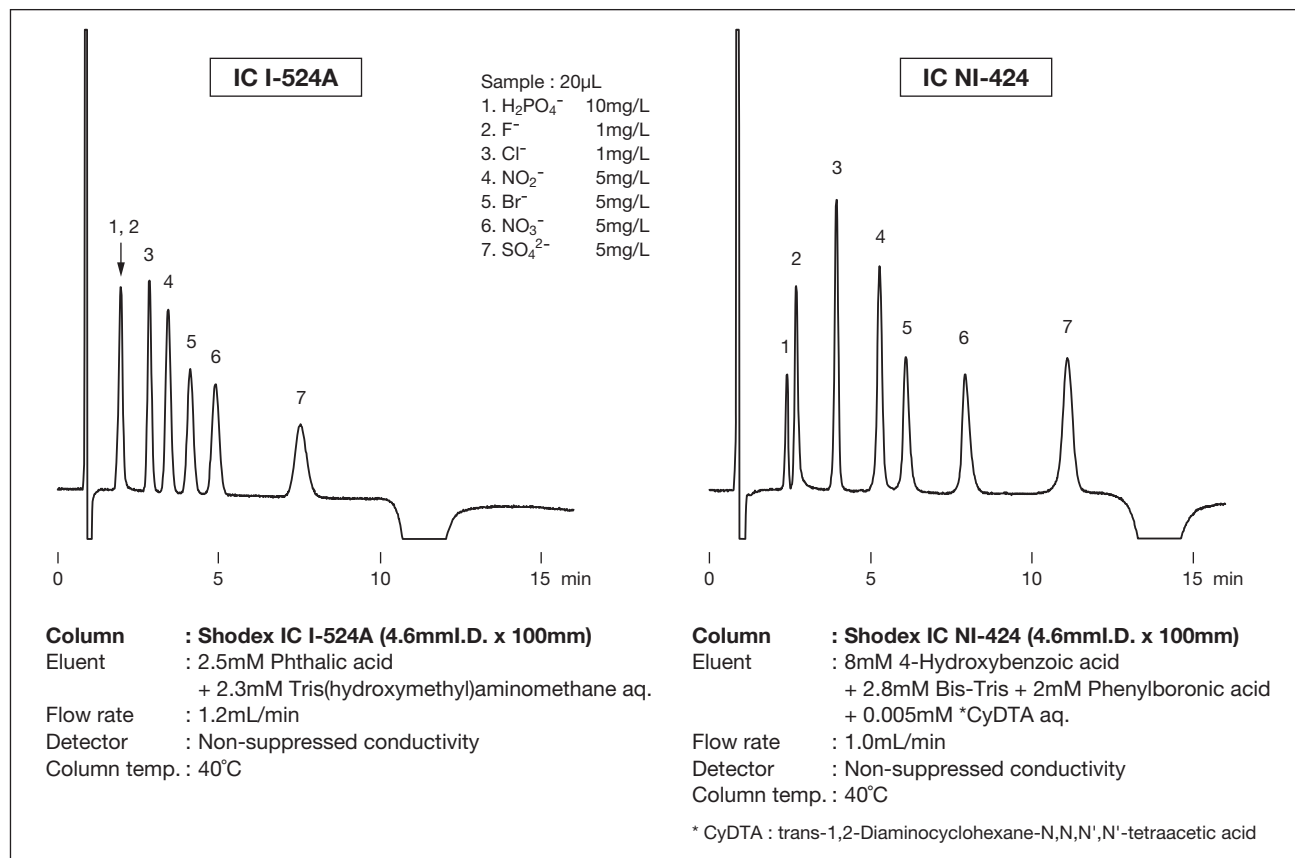


Fig. 3-10 Comparison of IC NI-424 and IC I-524A

Phthalate eluent improves the peak height to twice that achieved with hydroxybenzoate eluents, but six anions, from H_2PO_4^- to NO_3^- , elutes closely. (No.1-6 peaks in Figure 3-11).

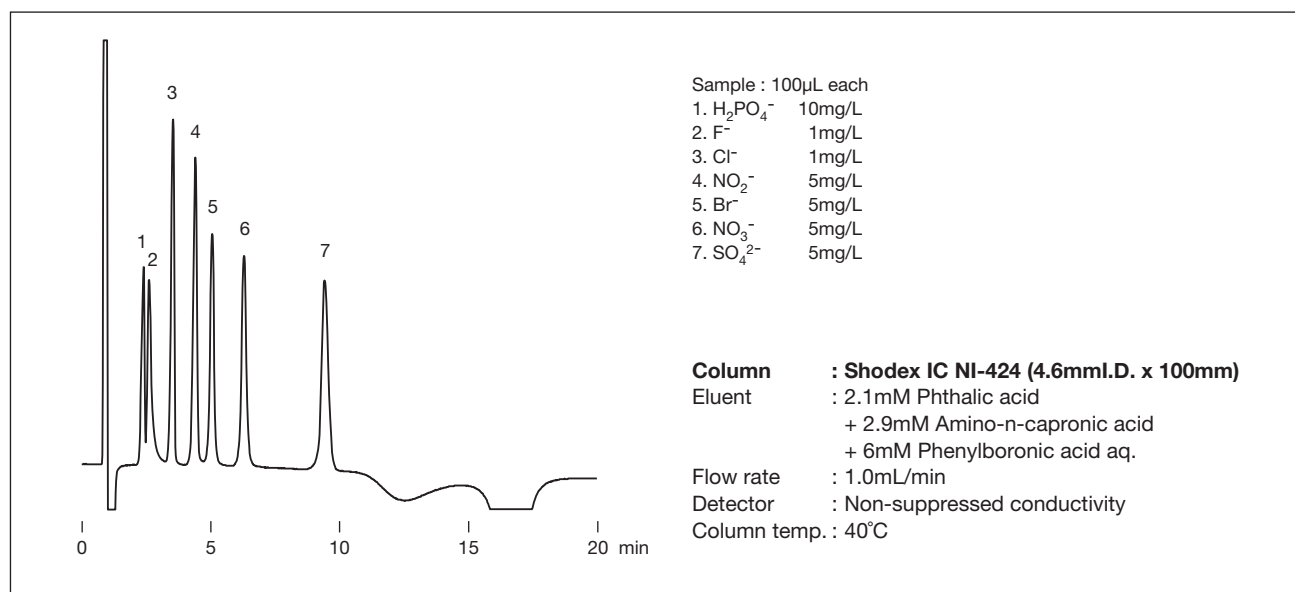


Fig. 3-11 Seven common anions analysis with phthalate eluents (IC NI-424)

IC NI-424 is not only capable of separating phosphate and fluoride ions but also capable of separating carbonate ion from phosphate.

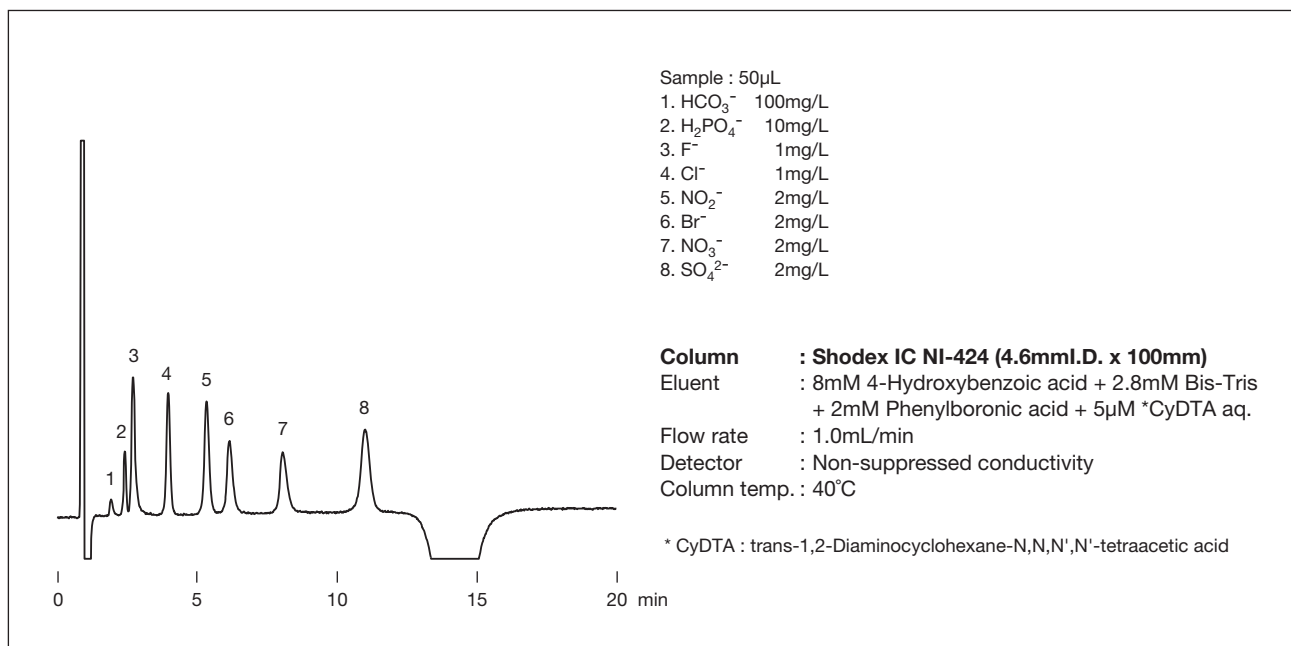


Fig. 3-12 Analysis of carbonate ion using IC NI-424

IC NI-424 is also suitable for the analysis of organic acids.

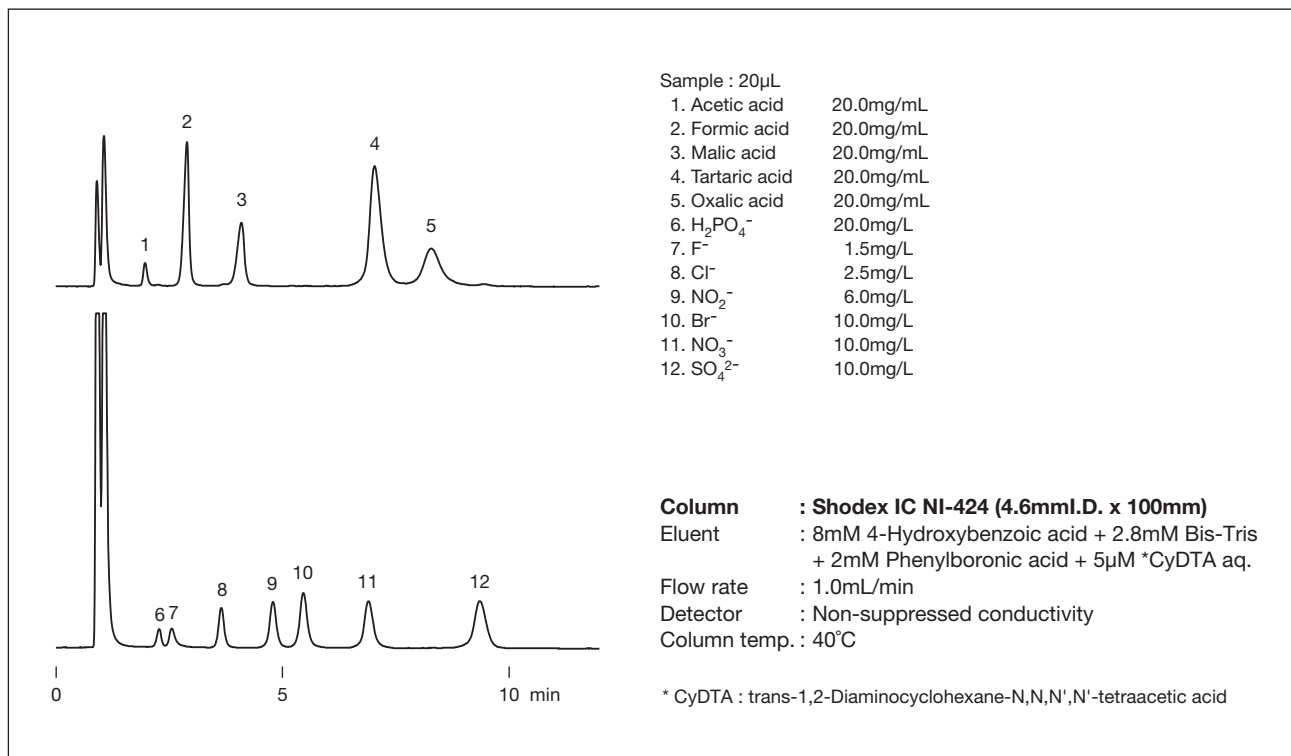


Fig. 3-13 Analysis of organic acids using IC NI-424

IC I-524A, a column for anion analysis, was used to separate nine anions including hydrophobic ions. Phthalate eluent is suitable for the acidic condition analysis. The response of phosphate ion is nearly eliminated under this condition.

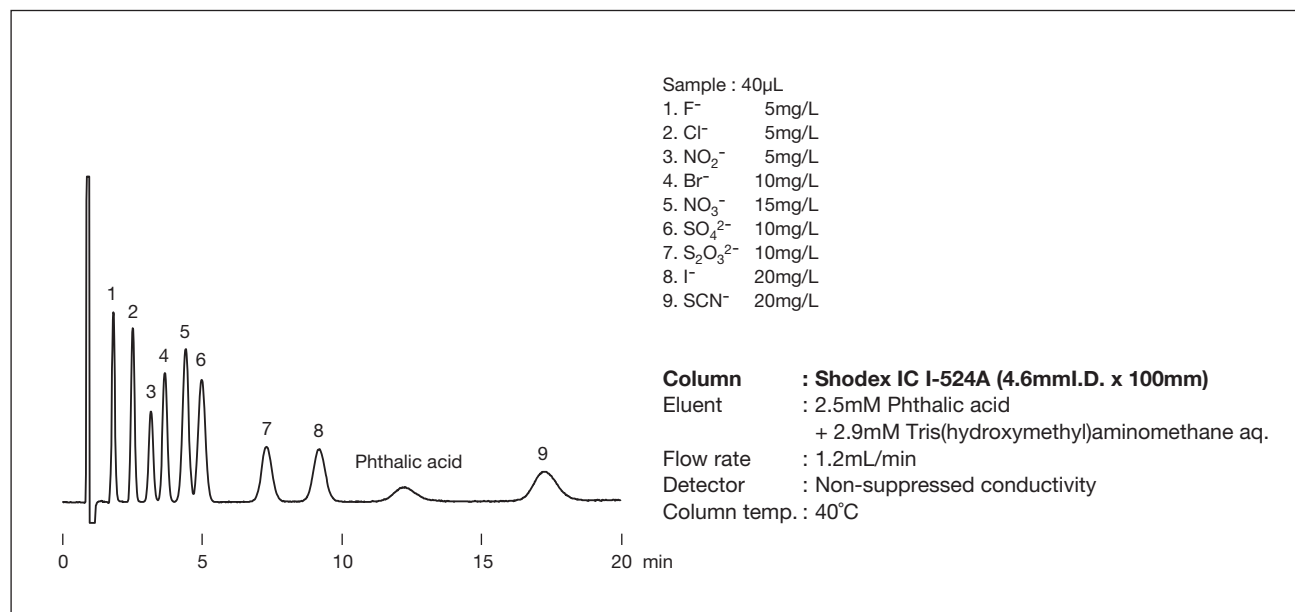


Fig. 3-14 Analysis of hydrophobic ions using IC I-524A

This example illustrates conditions ideal for separating ions that elute faster than the chloride ion when using the IC I-524A. Nitrate, sulfate, and other ions elute very slowly under this condition. When the sample to be analyzed contains these ions, 200 to 300 μ L of 0.1M tartaric acid must be injected after each sample analysis to remove any residual nitrate and other ions from the column.

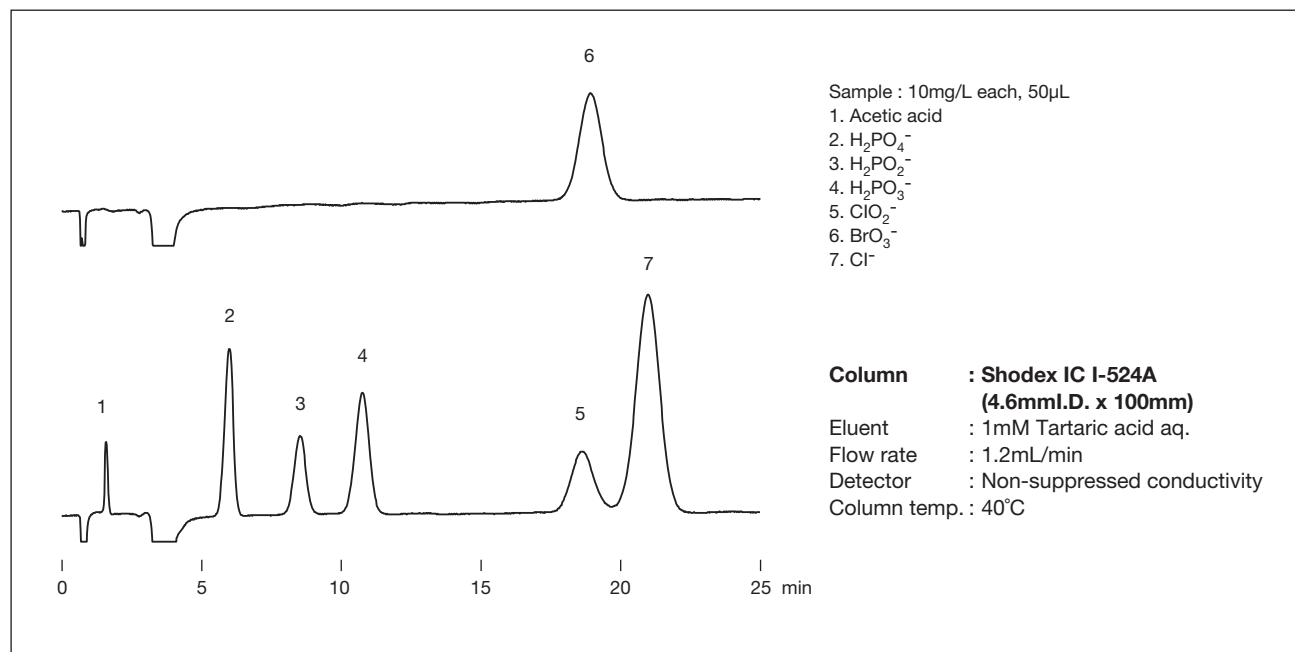


Fig. 3-15 Analysis of phosphate, hypophosphite and phosphate ions using IC I-524A

The carbonate ion, present in almost all aqueous samples, influences the ionic balance. The simultaneous analysis of the carbonate ion and seven common anions is thus an important part of ion chromatography.

IC SI-90 4E is a standard column for analysis with the suppressor method. In the following example, this column is used for high-sensitivity baseline separation of the carbonate ion and seven common anions with the non-suppressor method in a p-hydroxybenzoate eluent.

When the concentration of magnesium ion is 10mg/L or higher or the concentration of calcium ion is 20mg/L or higher under these conditions, these divalent cations form complexes with the components of the eluent. The complexes form broad peaks that overlap the peaks of target ions, making quantitative analysis difficult. To prevent this, the samples should be first passed through a pretreatment cartridge containing Na⁺ cation exchange resin to replace the divalent cations with sodium ions.

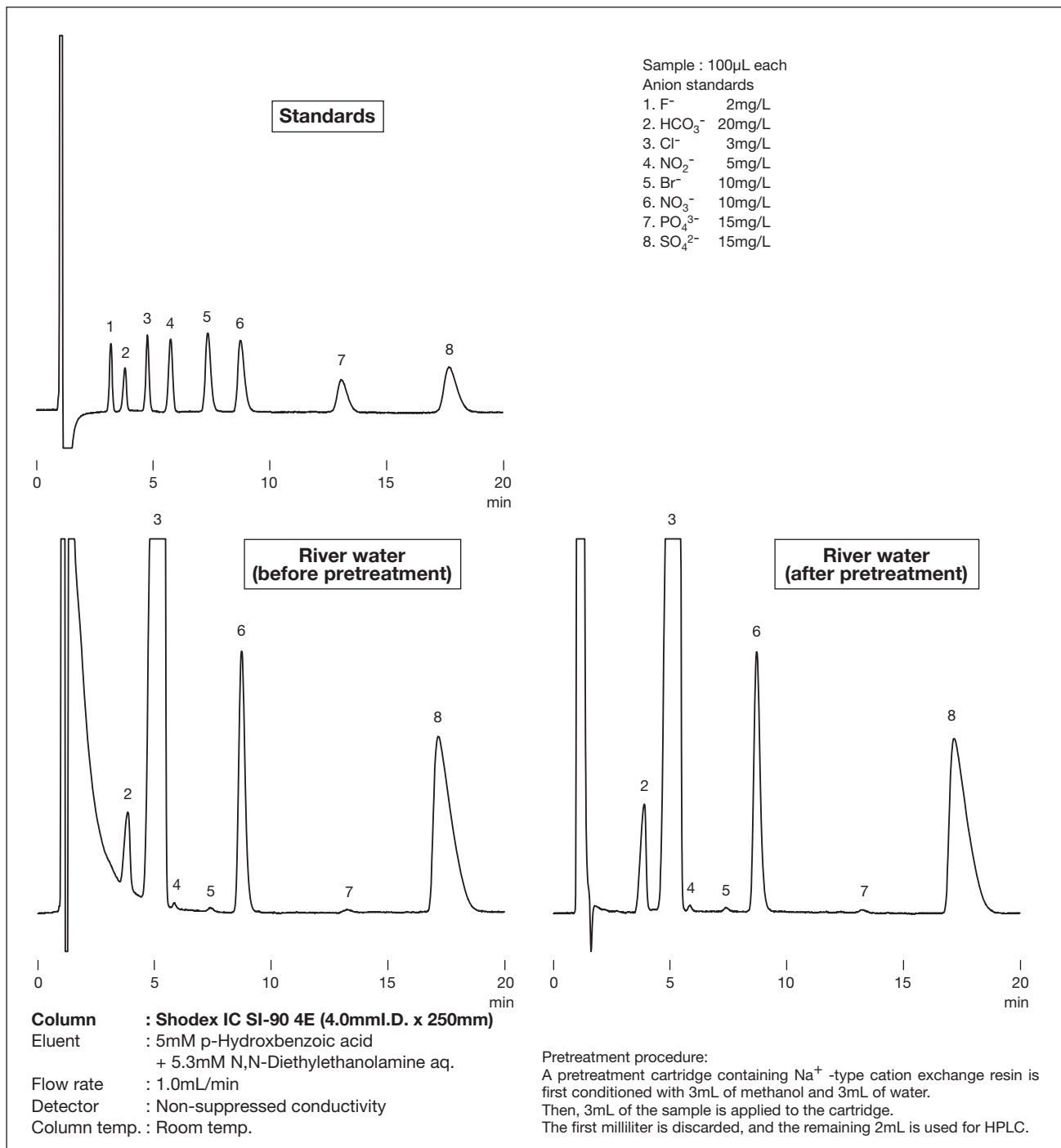


Fig. 3-16 Simultaneous analysis of carbonate ion and seven common anions

4. Cation analysis

The performance of IC YS-50 and IC YK-421, its predecessor of YS-50, were compared for the analysis of six common monovalent and divalent cations by non-suppressor method. IC YS-50 provided approximately 1.2-fold higher resolution for Na^+ and NH_4^+ than that of IC YK-421, and the theoretical plate number (N) for the divalent cations, the magnesium and calcium ions, was approximately 2-fold higher.

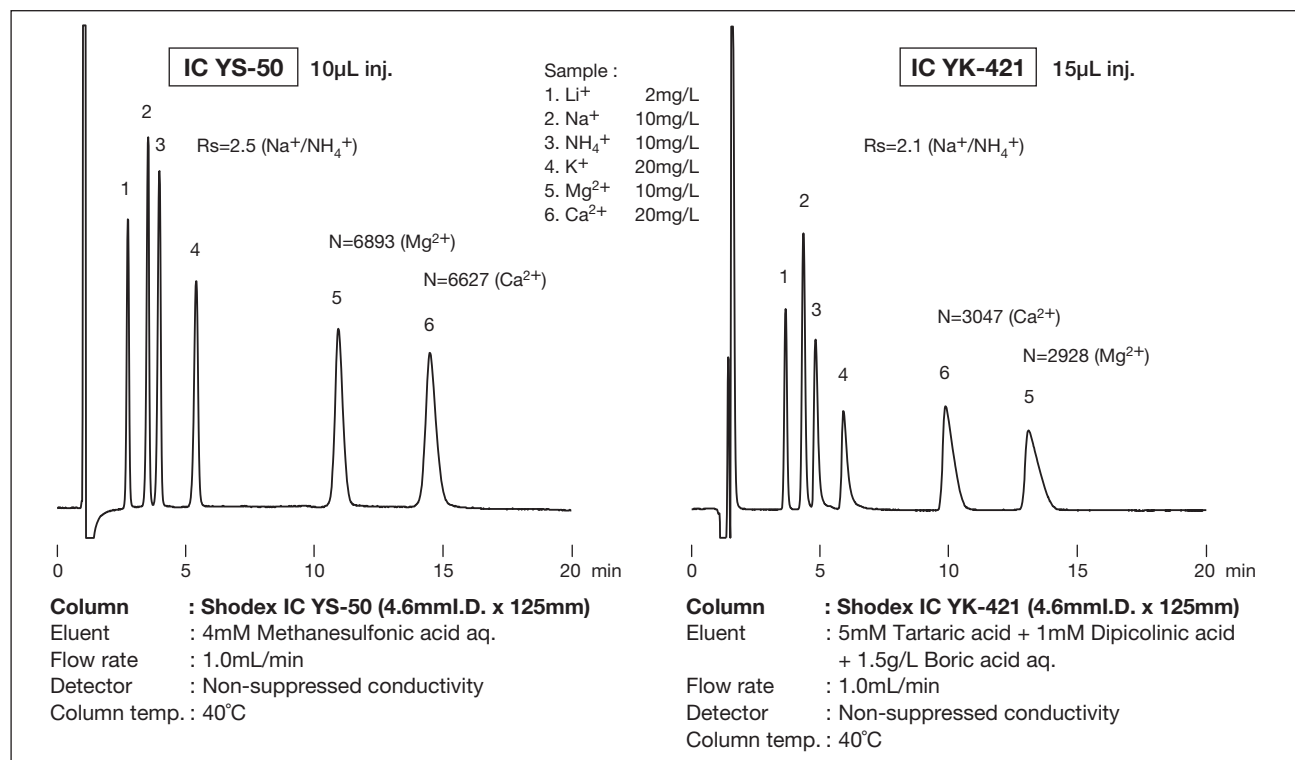


Fig. 4-1 Analysis of six common monovalent and divalent cations using IC YS-50 and IC YK-421

It is known that 18-Crown-6-ether forms complexes with cations. Formation of complex influences the elution of cations. Elution time of cations can be controlled by adding 18-Crown-6-ether to eluent. Potassium ions (K^+) form complexes more readily and show larger change in elution position than other cations. Addition of 18-Crown-6-ether controls K^+ elution, more over improves the separation of sodium (Na^+) and ammonium ions (NH_4^+)

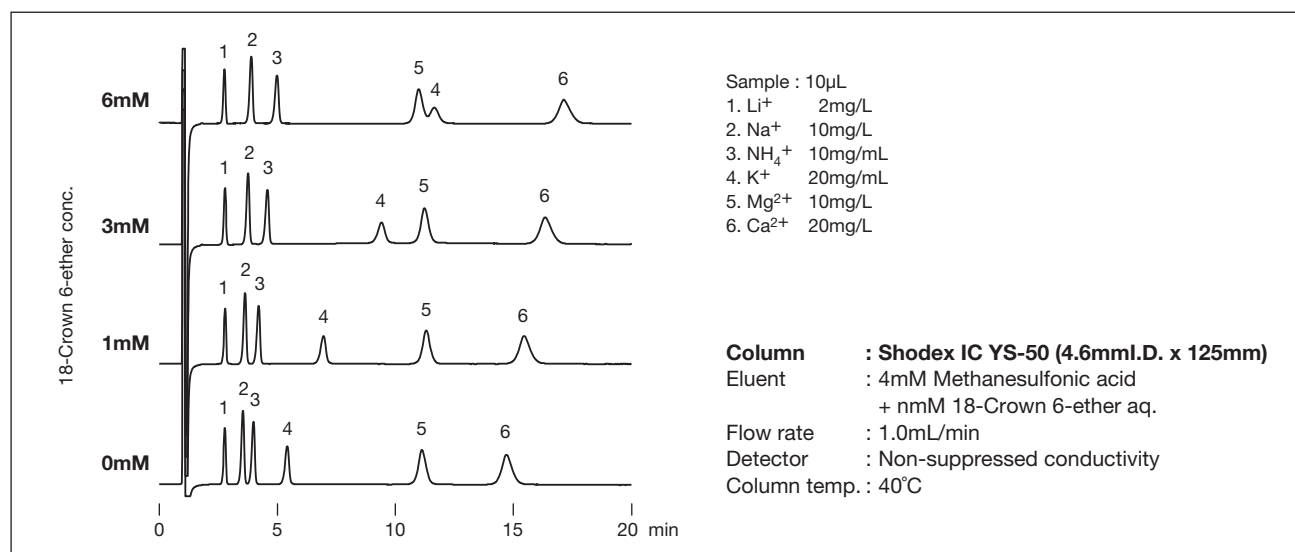


Fig. 4-2 Effect of 18-Crown-6-ether for cation separation using IC YS-50

IC YS-50 is generally used for simultaneous analysis of monovalent and divalent ions. By the use of an eluent containing 6mM tartaric acid and 4mM oxalic acid, the analysis of transition metal ions is also possible.

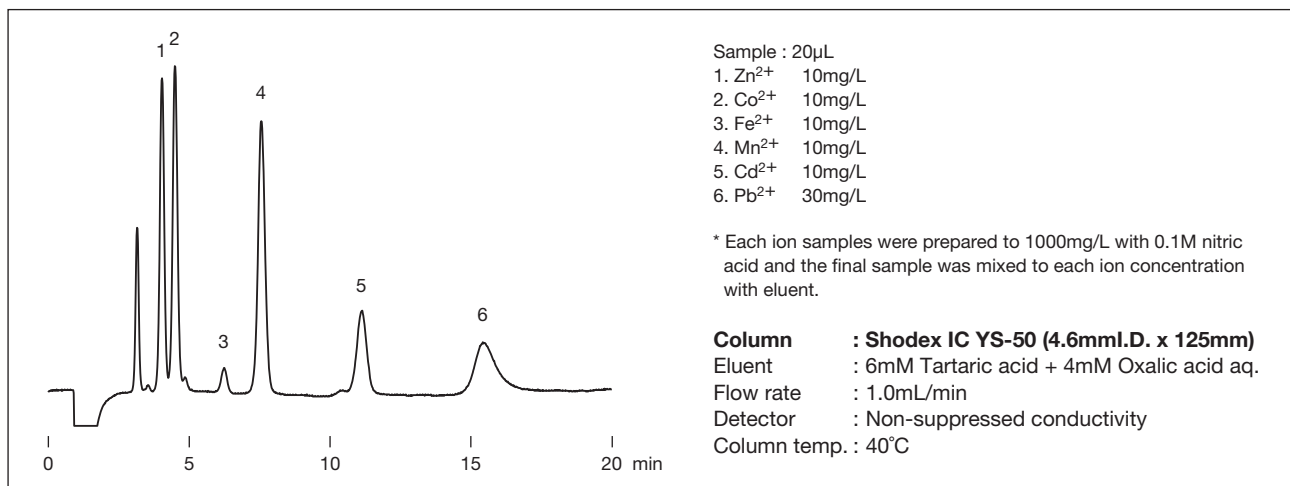


Fig. 4-3 Analysis of transition metal ions using IC YS-50

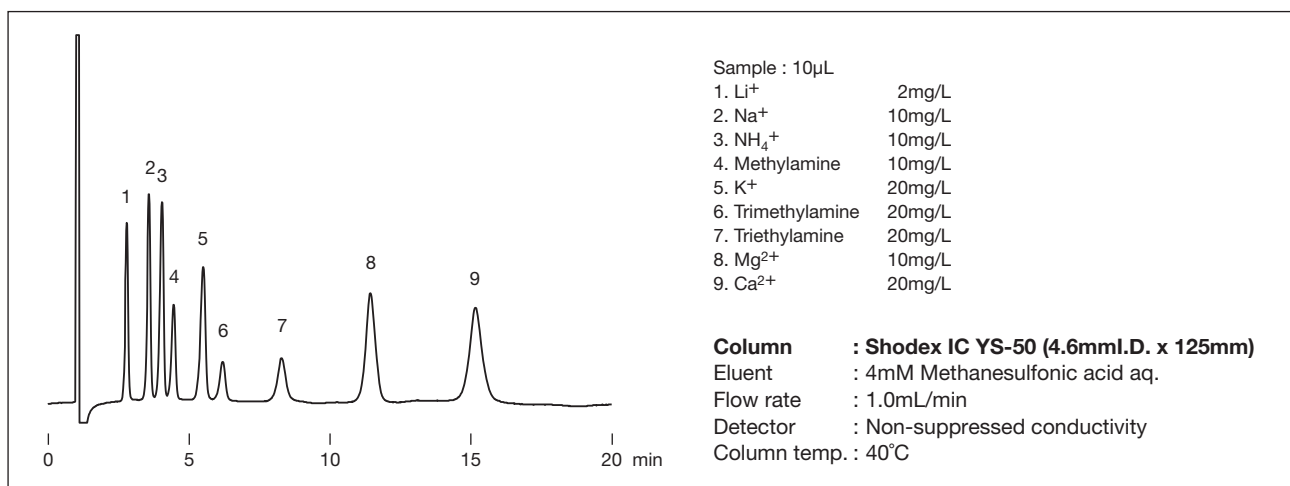


Fig. 4-4 Analysis of cations and alkyl amines using IC YS-50

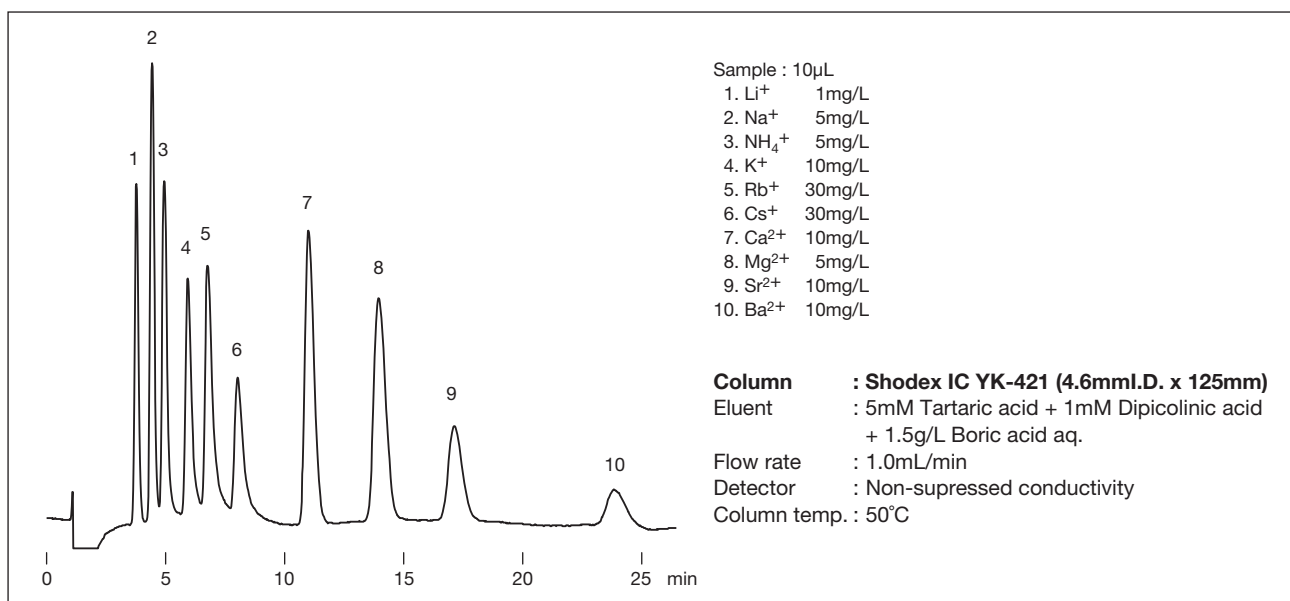


Fig. 4-5 Analysis of ten cations using IC YK-421

5. Applications

5-1. Environment

Ministerial Notification No.386 of the Japanese Ministry of Health, Labour and Welfare requires the addition of 1mL ethylenediamine solution (50mg/mL) to 1L of sample collected. This prevents chlorous acid from reacting with residual chlorine to form chloric acid. The following examples show analysis of anions, oxyhalides, and monovalent and divalent cations in tap water spiked with ethylenediamine.

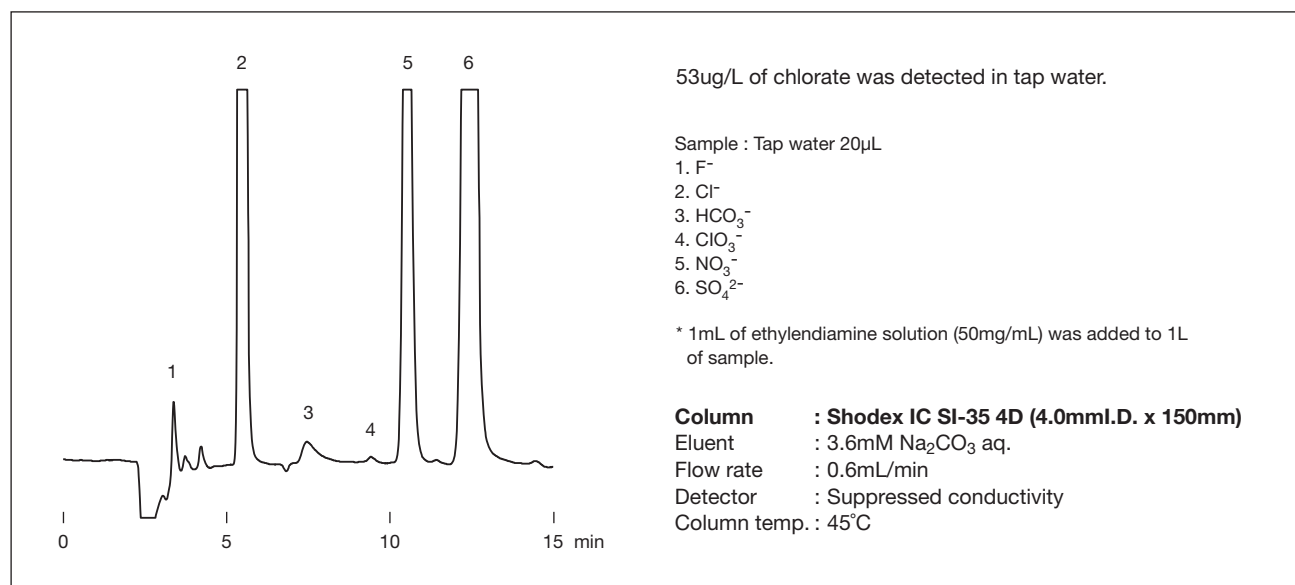


Fig. 5-1 Analysis of anions and oxyhalides in tap water using IC SI-35 4D

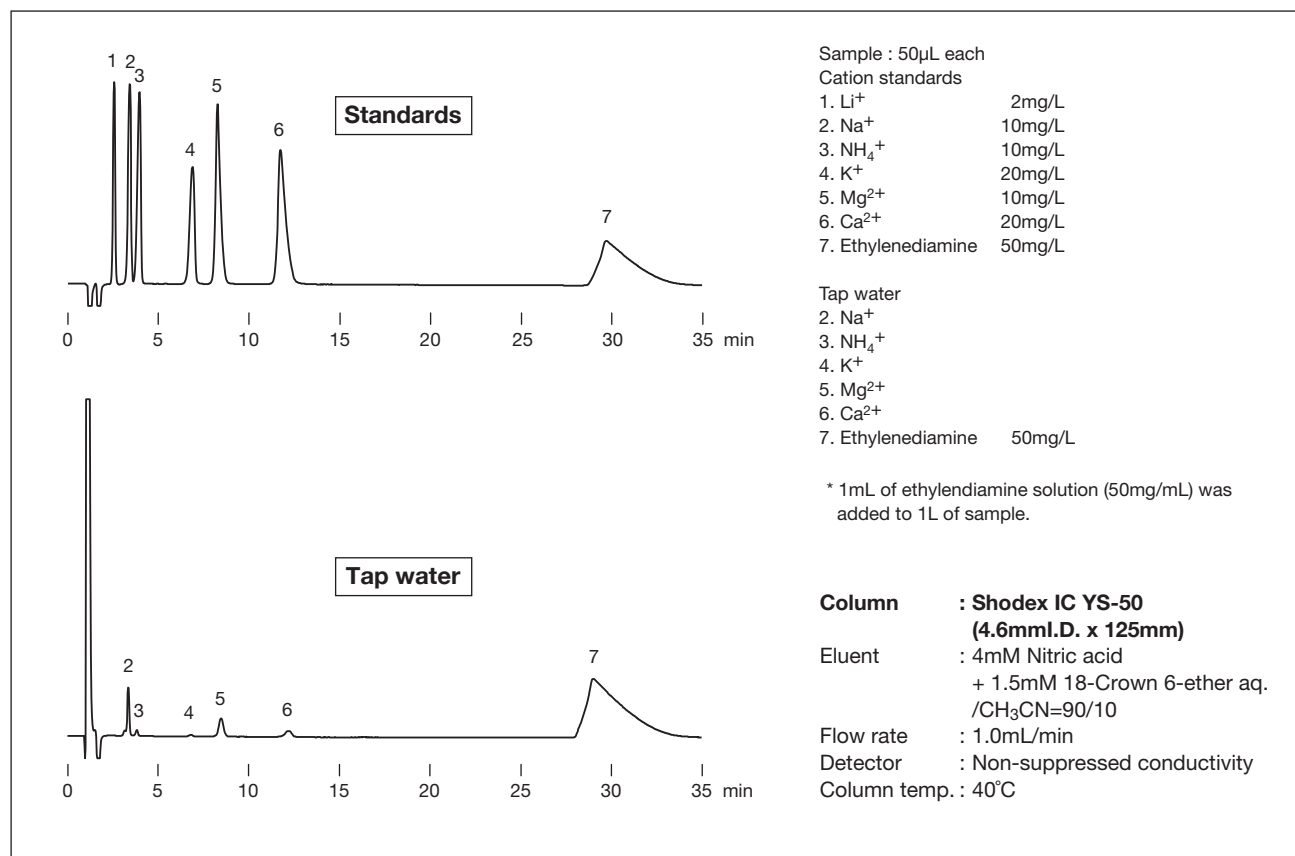


Fig. 5-2 Analysis of cations in tap water using IC YS-50

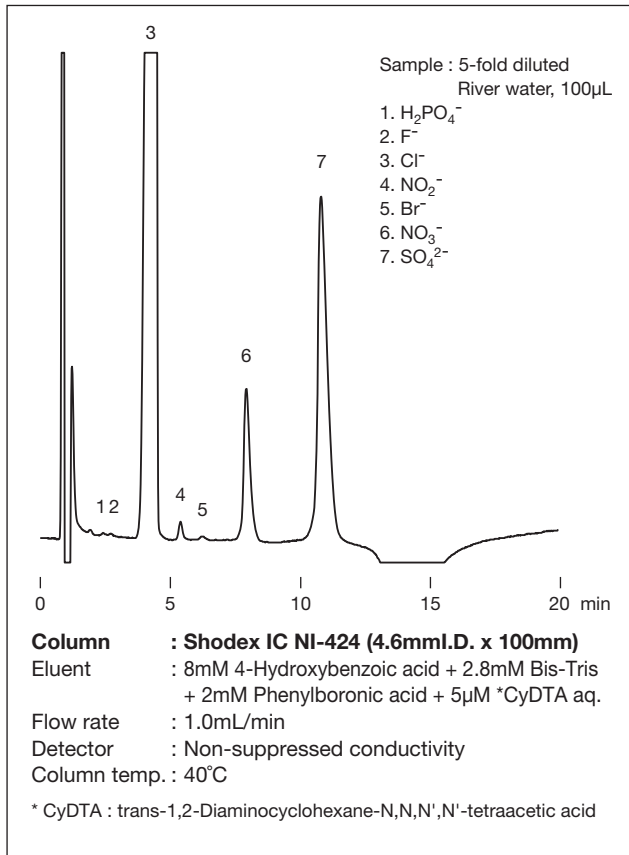


Fig. 5-3 Analysis of anions in river water

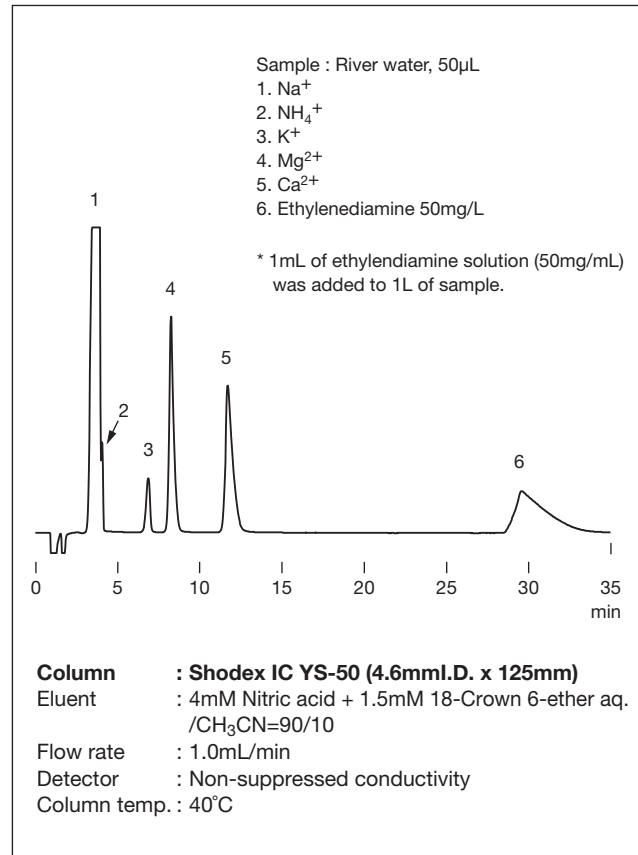


Fig. 5-4 Analysis of cations in river water

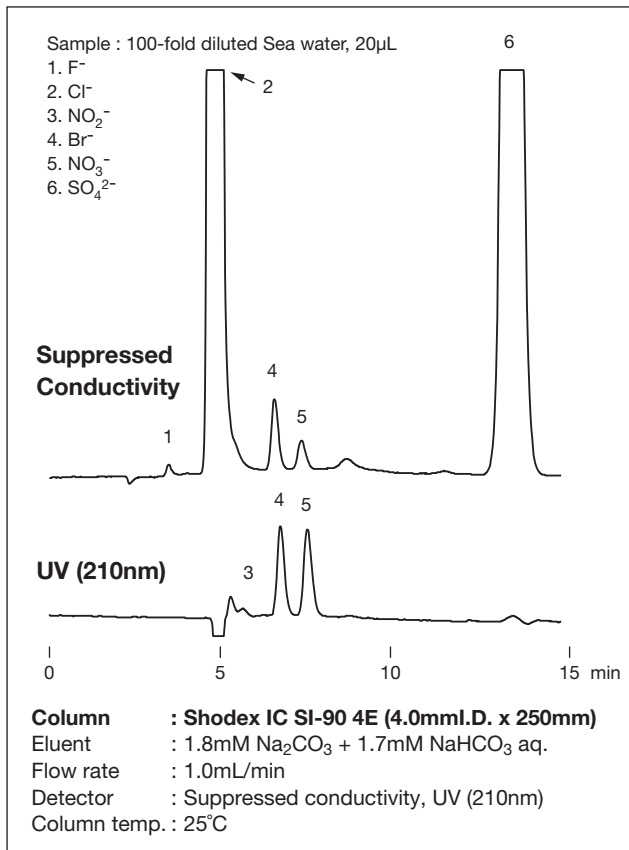


Fig. 5-5 Analysis of anions in sea water

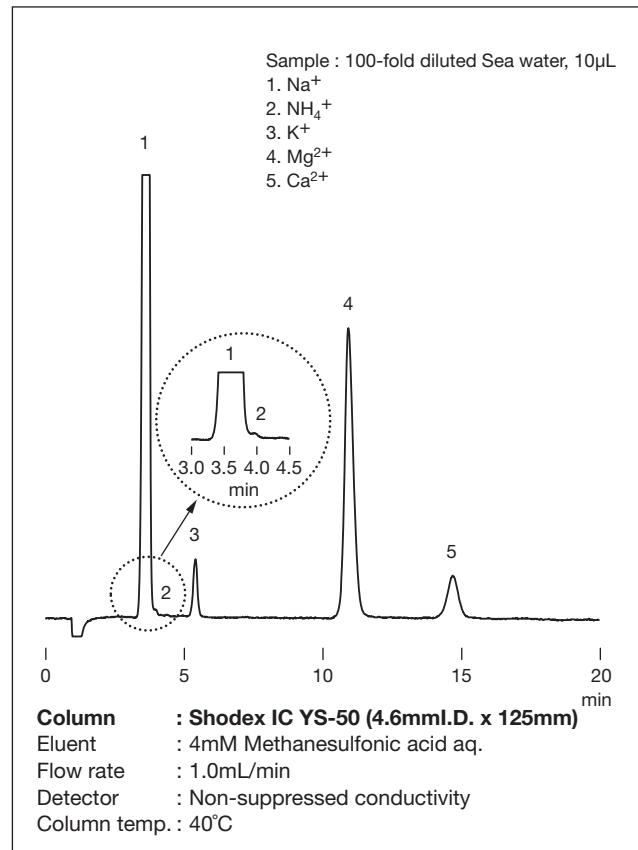


Fig. 5-6 Analysis of cations in sea water

5-2. Food

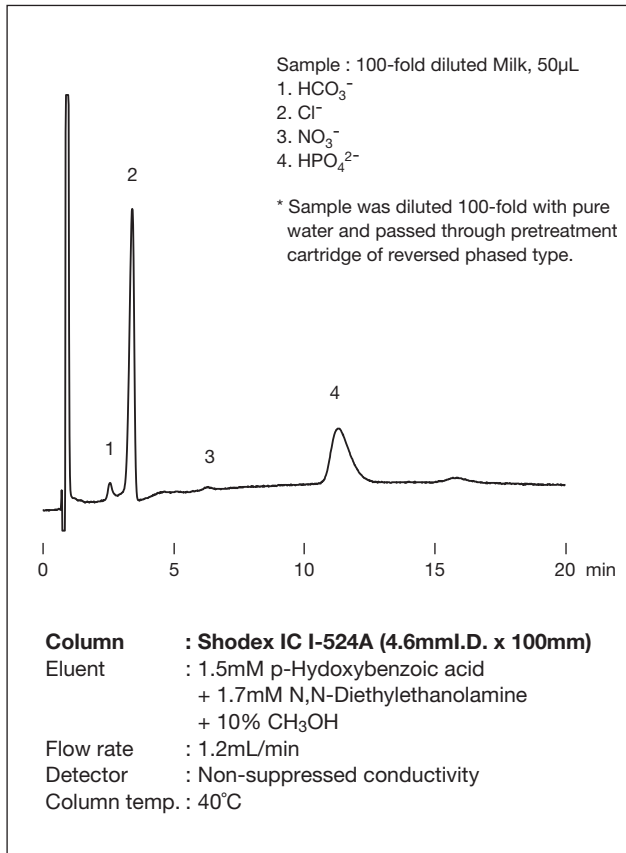


Fig. 5-7 Analysis of anions in milk

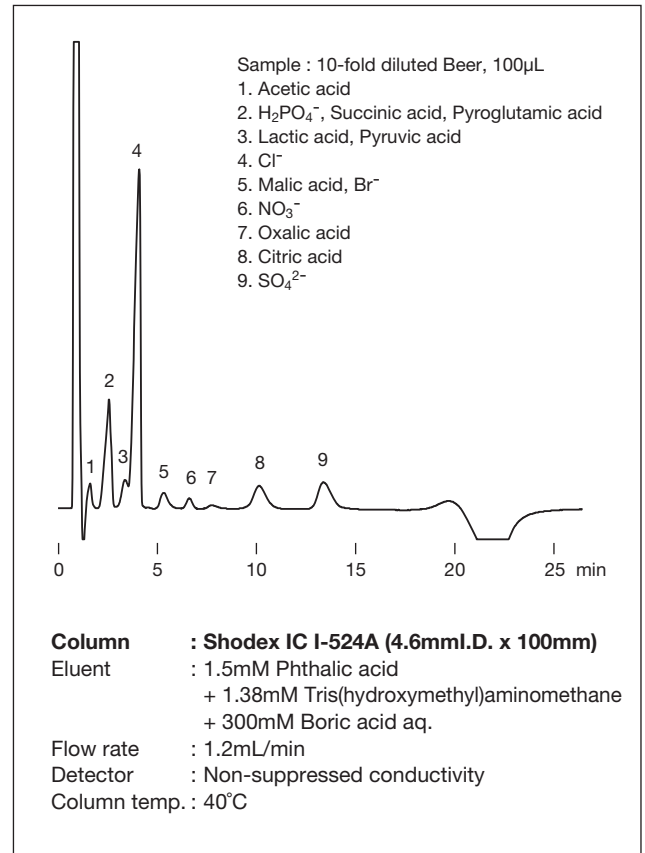


Fig. 5-8 Analysis of cations in beer

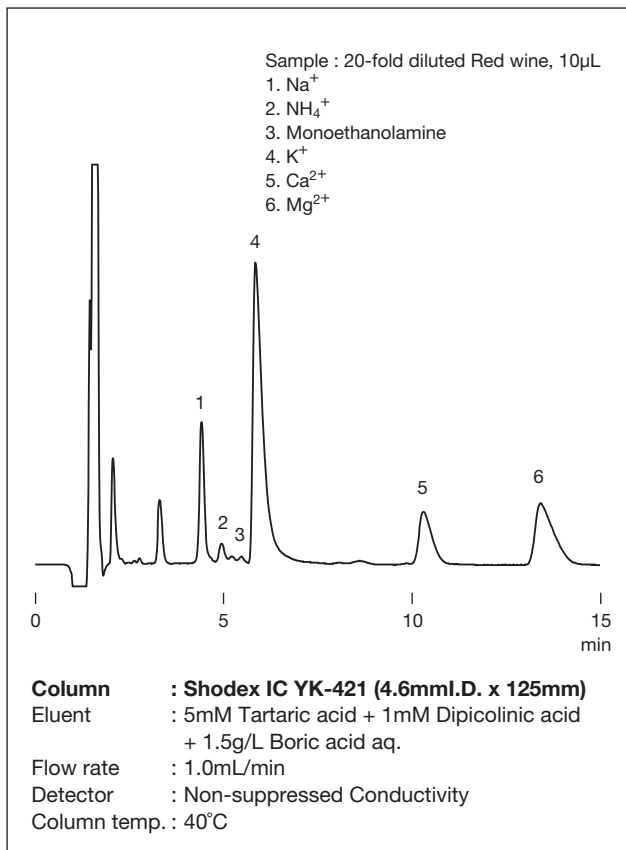


Fig. 5-9 Analysis of cations in red wine

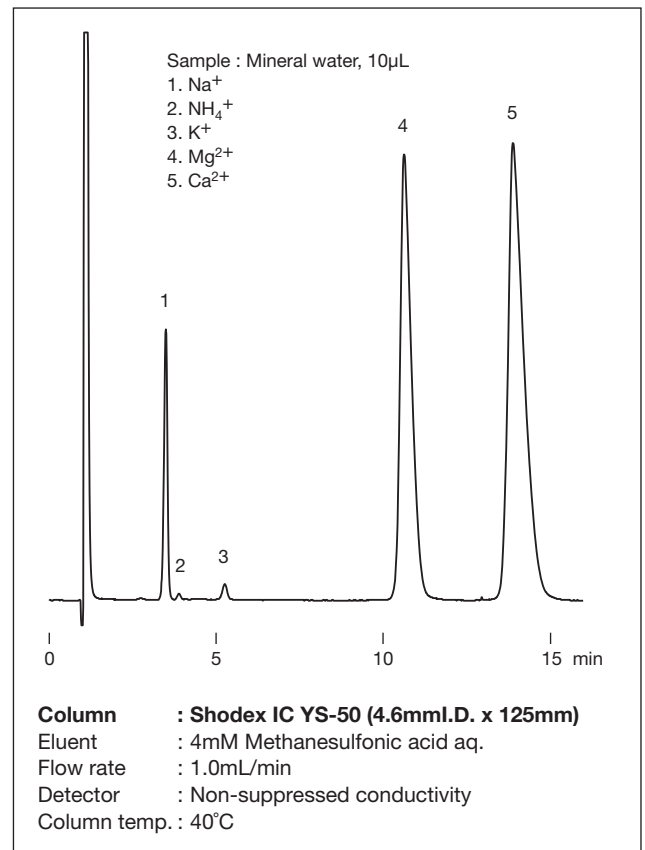


Fig. 5-10 Analysis of cations in mineral water

5-3. Others

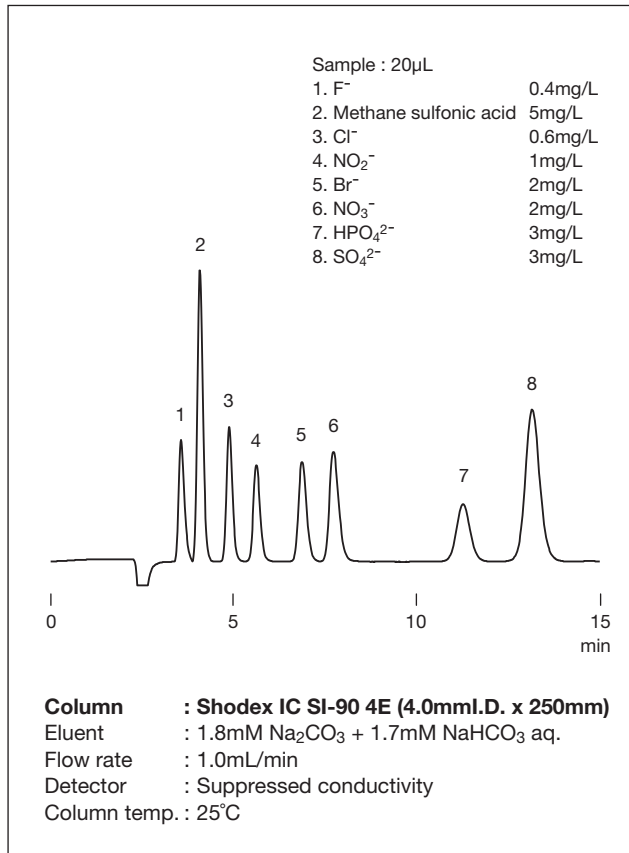


Fig. 5-11 Analysis of methane sulfonic acid using IC SI-90 4E

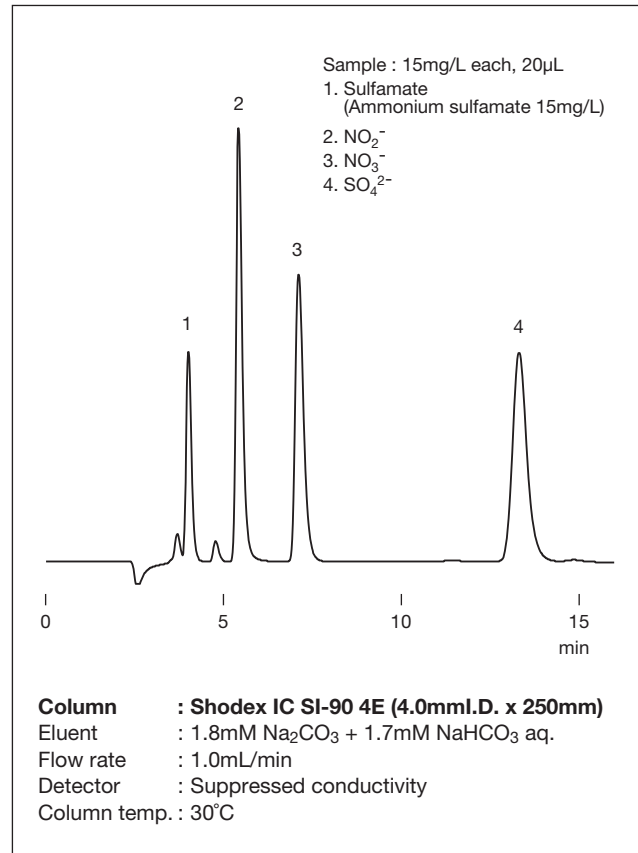


Fig. 5-12 Analysis of sulfamate using IC SI-90 4E

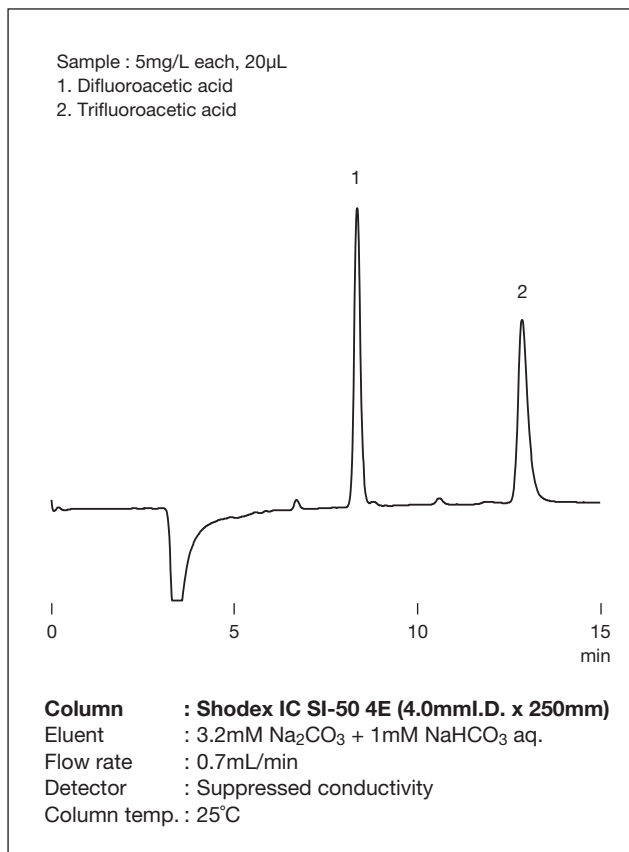


Fig. 5-13 Analysis of fluoroacetic acid using IC SI-90 4E

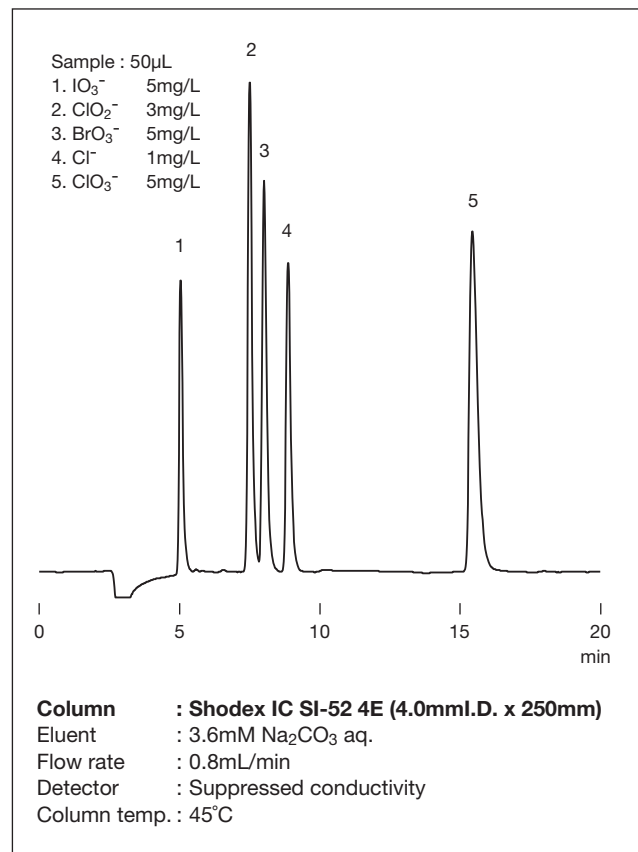


Fig. 5-14 Analysis of Iodate using IC SI-90 4E

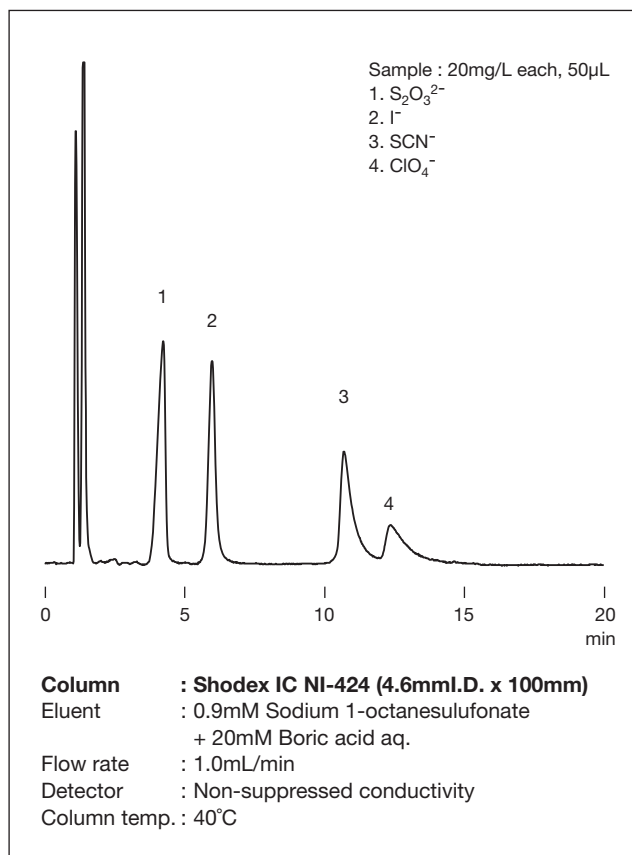


Fig. 5-15 Analysis of hydrophobic anions using IC NI-424

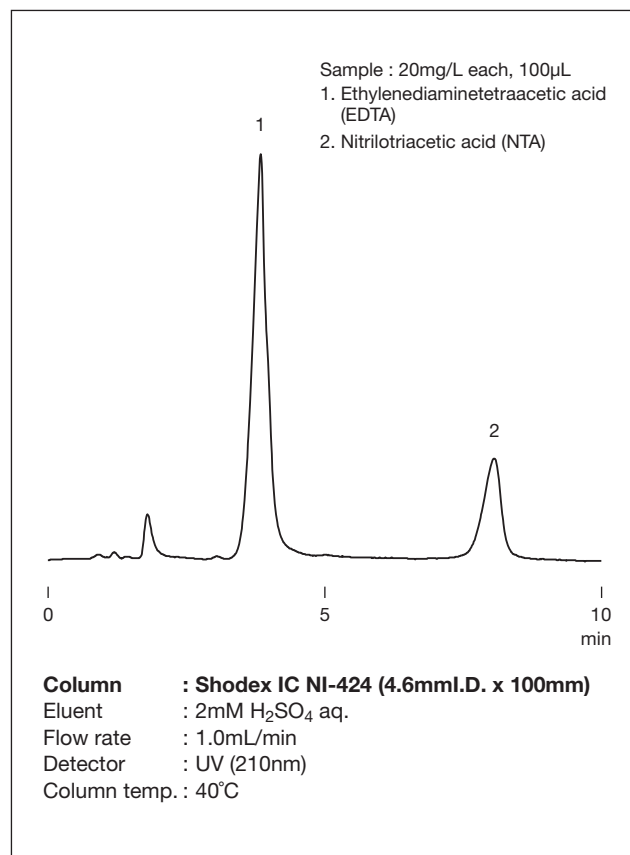


Fig. 5-16 Analysis of chelating agents using IC NI-424

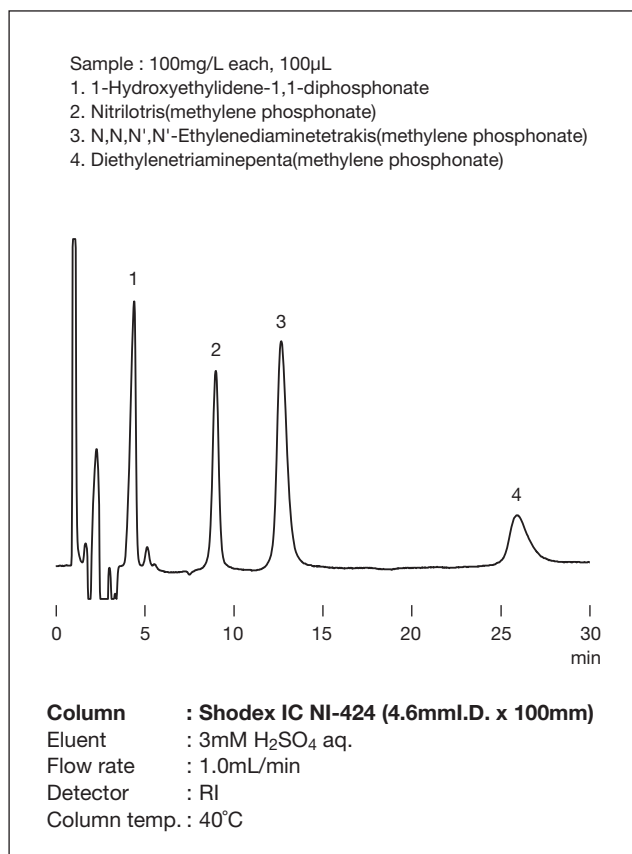


Fig. 5-17 Analysis of phosphonic acids using IC NI-424

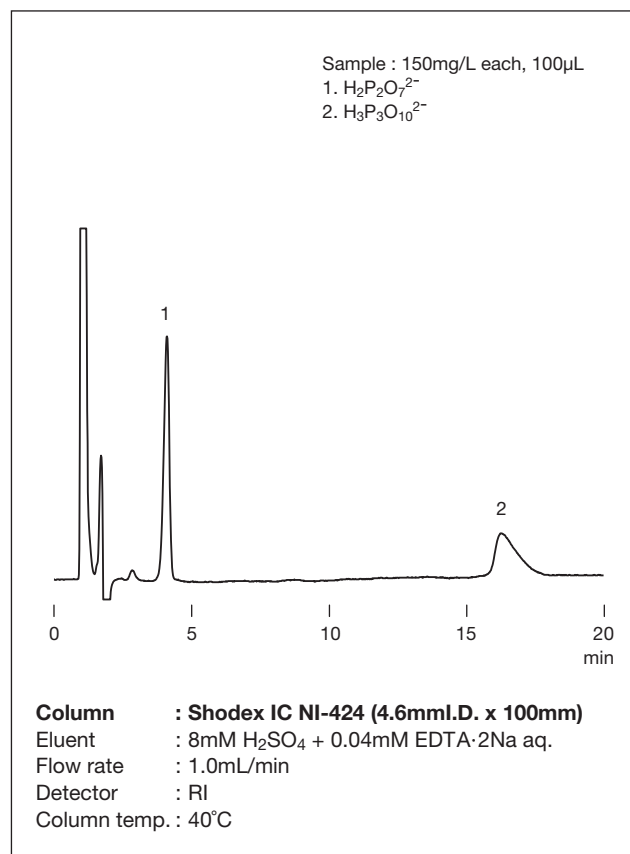


Fig. 5-18 Analysis of pyrophosphoric acid and tripolyphosphate using IC NI-424

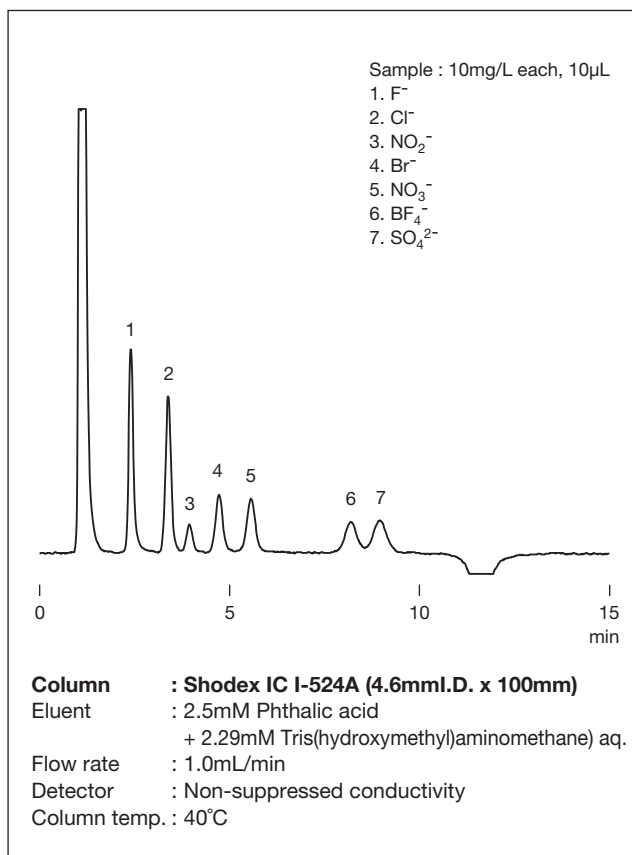


Fig. 5-19 Analysis of tetrafluoroborate using IC I-524A

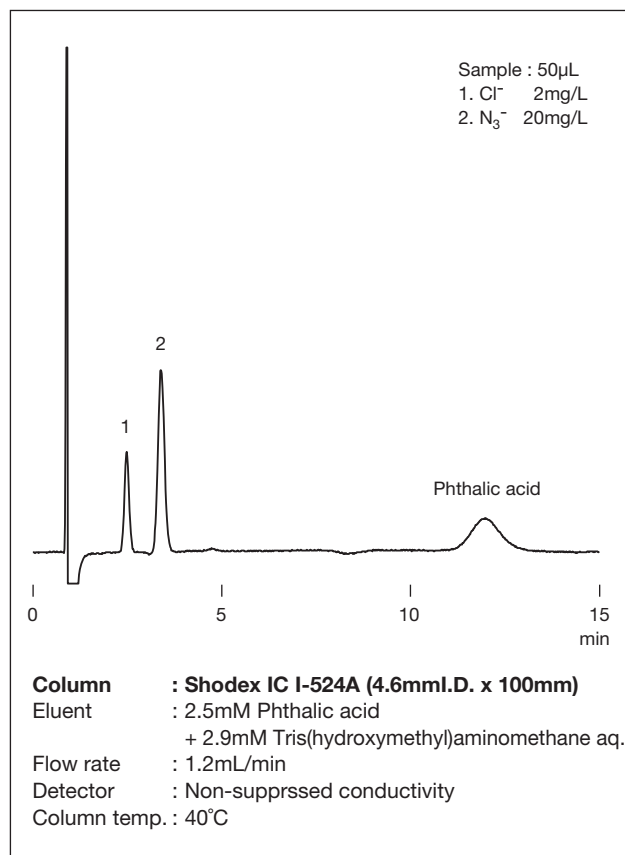


Fig. 5-20 Analysis of azide using IC I-524A

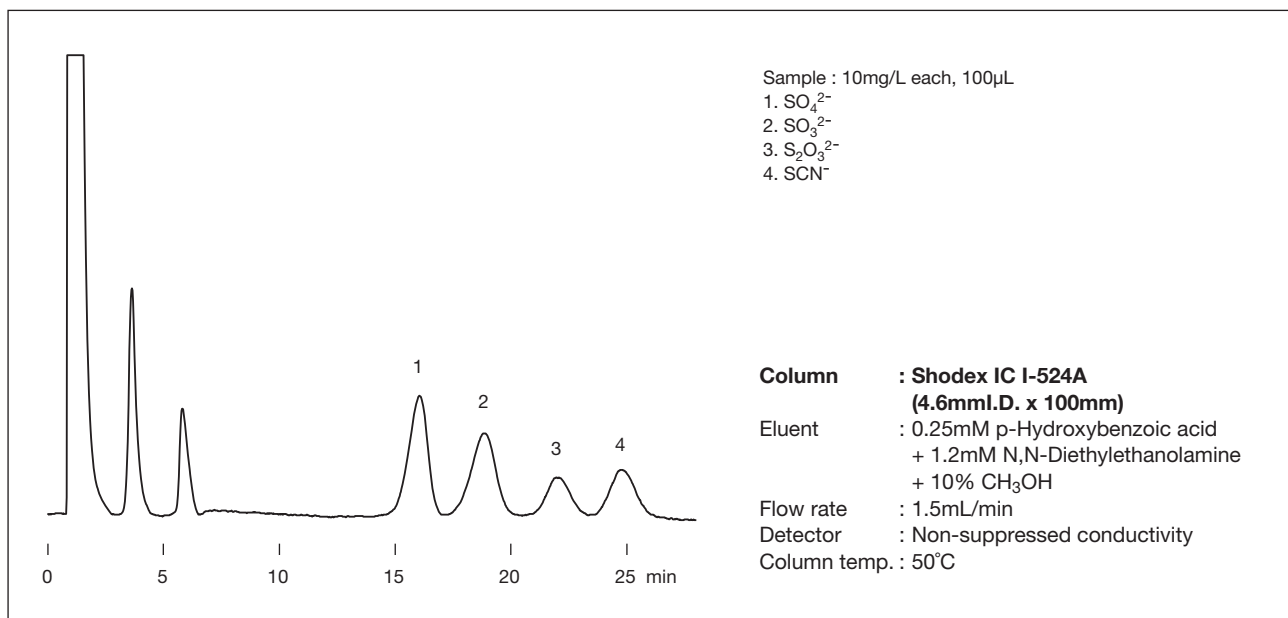


Fig. 5-21 Analysis of sulfate, sulfite, thiosulfate and thiocyanate using IC I-524A

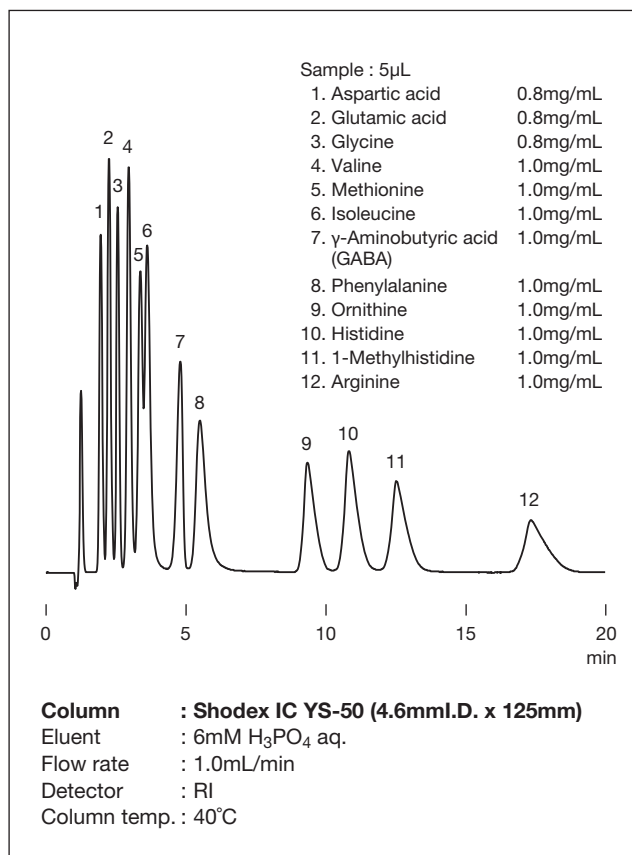


Fig. 5-22 Analysis of amino acids using IC YS-50

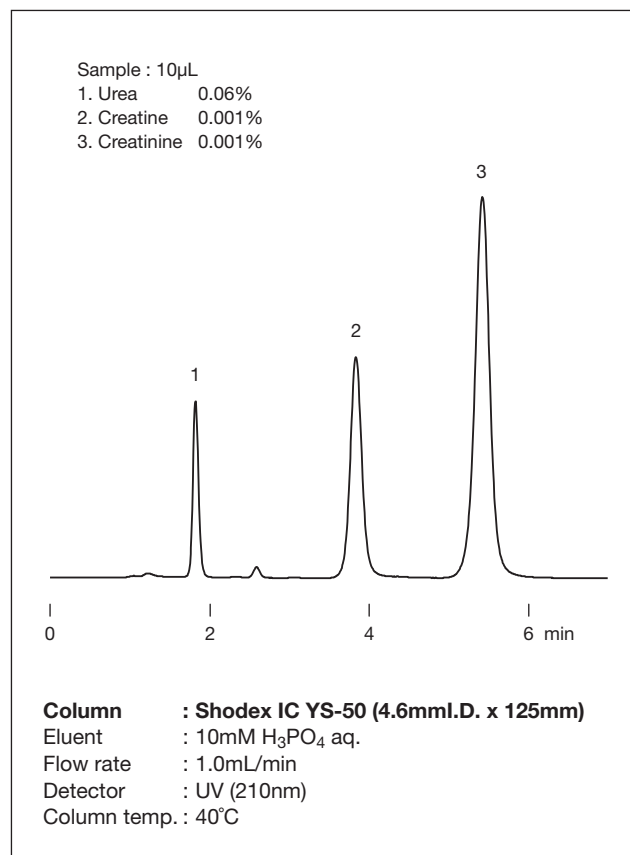


Fig. 5-23 Analysis of metabolite of nitrogenous substances using IC YS-50

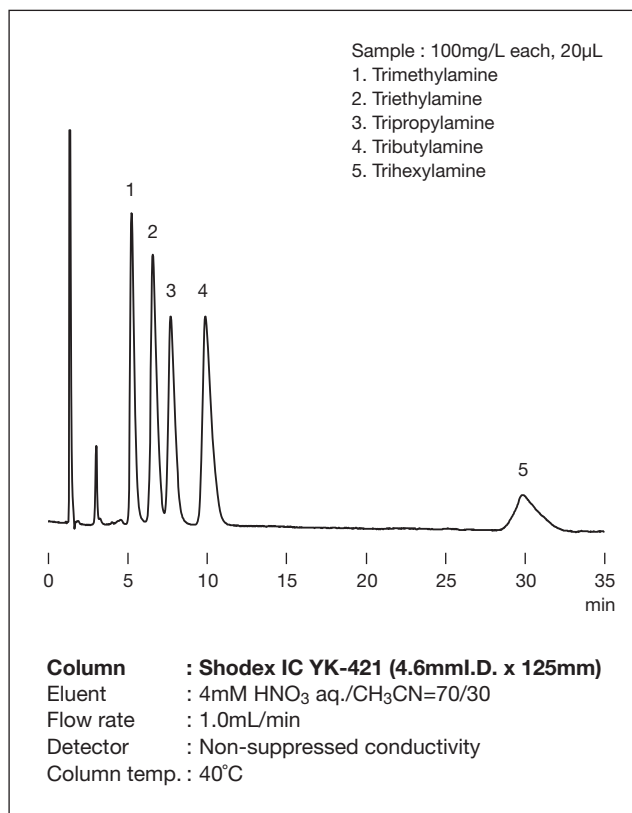


Fig. 5-24 Analysis of trialkylamines using IC YK-421

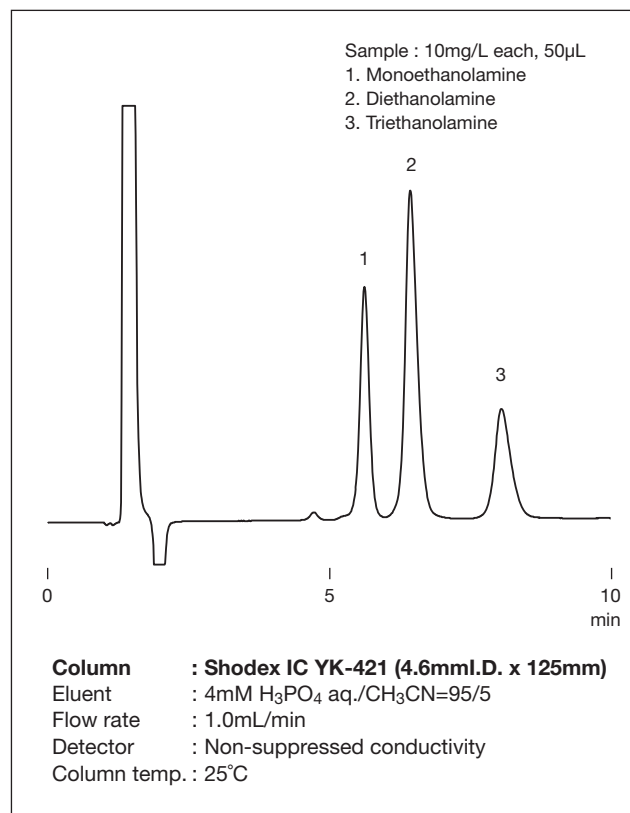


Fig. 5-25 Analysis of ethanolamines using IC YK-421