

Simultaneous Analysis of Anions and Cations Using Ion Chromatograph Dual Channel System

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User Benefits

- ◆ Simultaneous analysis of anions and cations in a single sample can be done.
- ◆ Traceability can be ensured by managing anion and cation analytical results in one data file.
- ◆ Excellent repeatability and low contamination were provided by loop injection method.

Introduction

When a single ion chromatograph is used to analyze both anions and cations, it is necessary to change the analytical conditions. The flow path cleaning and the column replacement required in every mobile phase switching are tedious and time consuming whereas those are not apparently shown in the analytical results.

The ion chromatograph dual channel system enables simultaneous analysis of anions and cations. For anions, suppressor and non-suppressor methods can be selected, and UV-VIS detector can be used for the suppressor method.

This article introduces applications obtained by a combination of anion analysis with an electrodiagnosis-type suppressor system HIC-ESP and cation analysis with a non-suppressor system.

Flow Path Diagram

Fig. 1 shows the flow path diagram of this system. Both sample loops in the anion and cation analysis channels are filled with the sample by a single injection, and the analysis starts by switching both injection valves simultaneously. The results of anion and cation analyses are stored in one data file. Therefore, data management and report output can be performed easily, and traceability is also ensured.

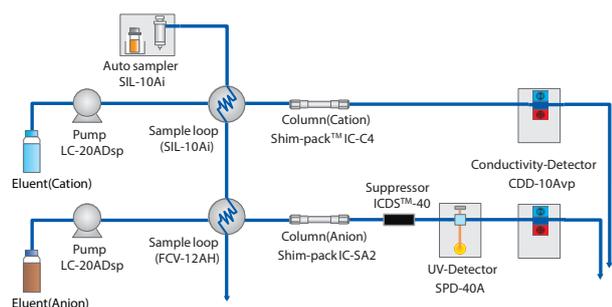


Fig. 1 HIC-ESP/NS Ion Chromatograph Dual Channel System Flow Path Diagram

Analysis of Standard Samples

Analysis was carried out using Shim-pack IC-SA2 column for anions and Shim-pack IC-C4 column for cations. Table 1 shows the analytical conditions. Mobile phase composition and flow rate can be changed according to the analytical purpose, but since the column oven is shared with anion analysis channel and cation analysis channel, the temperature condition must be set to the same value. In this system, the sampling volume is set to 1600 μL to completely displace the two sample loops with standard solution, but the actual injection volume is determined by the sample loop volume (50 μL each, here). Table 2 shows composition of anion standard mixture, and its chromatograms are shown in Fig. 2. Table 3 shows composition of cation standard mixture, and its chromatograms are shown in Fig. 3. Chromatograms of counter ions contained in each mixture are also shown in Fig.2 and Fig.3.

Table 1 analytical conditions

Anion	
Column	: Shim-pack IC-SA2 (250 mm \times 4.0 mm I.D., 9 μm) ^{*1} : Shim-pack IC-SA2(G) (10 mm \times 4.6 mm I.D., 9 μm) ^{*2}
Mobile Phase	: 12 mmol/L sodium hydrogen carbonate, 0.6 mmol/L sodium carbonate
Flow Rate	: 1.0 mL/min
Cation	
Column	: Shim-pack IC-C4 (150 mm \times 4.6 mm I.D., 7 μm) ^{*3} : Shim-pack IC-GC4 (10 mm \times 4.6 mm I.D., 7 μm) ^{*4}
Mobile Phase	: 2.5 mmol/L oxalic acid
Flow Rate	: 1.0 mL/min
Column Temp.	: 40 $^{\circ}\text{C}$
Injection Vol.	: 50 μL ea. (Setting : 1600 μL)
Vial	: Shimadzu Vial, LC, 4 mL, Polypropylene ^{*5}
Detection	: Conductivity, UV-VIS (210 nm)

*1 P/N : 228-38983-91, *2 P/N : 228-38983-92, *3 P/N : 228-41616-91

*4 P/N : 228-59900-91, *5 P/N : 228-31537-91

Table 2 Composition of Anion Standard Mixture

F ⁻	Fluoride ion	0.025 mg/L
Cl ⁻	Chloride ion	0.025 mg/L
NO ₂ ⁻	Nitrite ion	0.1 mg/L
Br ⁻	Bromide ion	0.1 mg/L
NO ₃ ⁻	Nitrate ion	0.1 mg/L
PO ₄ ³⁻	Phosphate ion	0.25 mg/L
SO ₄ ²⁻	Sulfate ion	0.1 mg/L

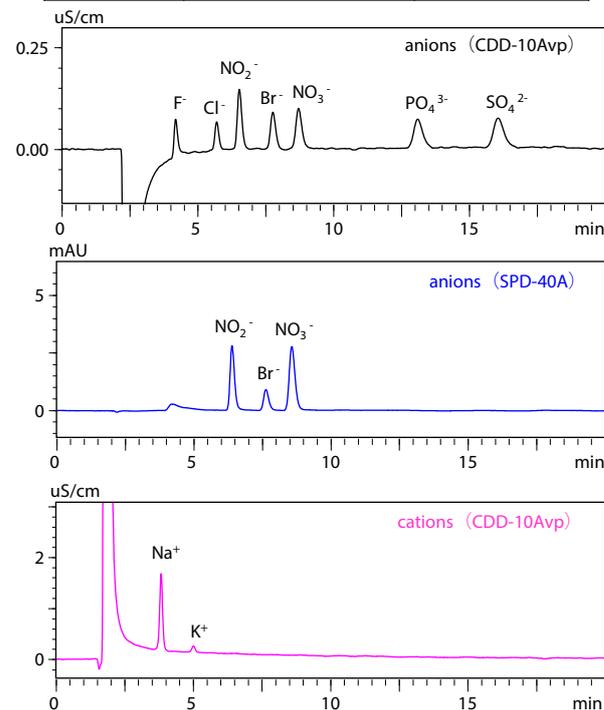


Fig. 2 Chromatograms of Anion standard Mixture

Table 3 Composition of Cation Standard Mixture

Li ⁺	Lithium ion	0.01 mg/L
Na ⁺	Sodium ion	0.04 mg/L
NH ₄ ⁺	Ammonium ion	0.04 mg/L
K ⁺	Potassium ion	0.1 mg/L
Mg ²⁺	Magnesium ion	0.1 mg/L
Ca ²⁺	Calcium ion	0.1 mg/L

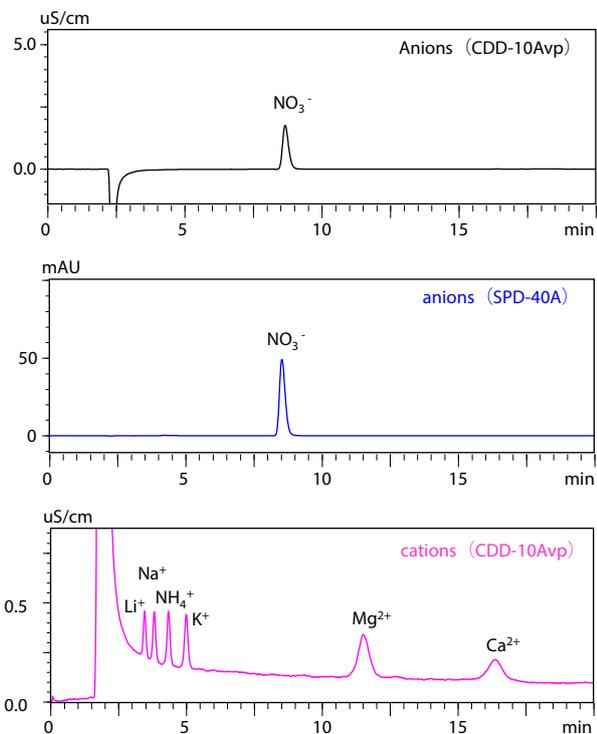


Fig. 3 Chromatograms of Cation standard Mixture

Area Repeatability and Lower Limit of Quantification

Table 4 shows the area repeatabilities (%RSD) and the lower limits of quantification of 6 repeated analyses of each standard mixture in Fig. 2 and Fig. 3. Each lower limit of quantification (LOQ, mg/L) was calculated as the concentration at which S/N ratio was 10.

Table 4 Area repeatability (n=6) and lower limit of quantification

	concentration (mg/L)	area repeatability (%RSD)	LOQ (mg/L)
F ⁻	0.025	2.45	0.008
Cl ⁻	0.025	2.30	0.011
NO ₂ ⁻	0.1	2.20	0.021
Br ⁻	0.1	1.34	0.034
NO ₃ ⁻	0.1	2.88	0.031
PO ₄ ³⁻	0.25	2.48	0.11
SO ₄ ²⁻	0.1	3.53	0.042
NO ₂ (UV-VIS)	0.1	0.35	0.003
Br ⁻ (UV-VIS)	0.1	0.52	0.009
NO ₃ ⁻ (UV-VIS)	0.1	0.41	0.003
Li ⁺	0.01	1.26	0.003
Na ⁺	0.04	1.89	0.010
NH ₄ ⁺	0.04	2.65	0.009
K ⁺	0.1	1.82	0.022
Mg ²⁺	0.1	3.05	0.028
Ca ²⁺	0.1	3.78	0.062

Coefficient of Determination

7-point calibration curves were created for each ion. Table 5 shows the calibration ranges and the coefficients of determination of each calibration curve created by linear regression. All ions have good linearities.

Table 5 Calibration Curve Range and coefficient of determination

	Range (mg/L)	Contribution Rate (r ²)
F ⁻	0.01 - 1	0.9999
Cl ⁻	0.01 - 1	1.0000
NO ₂ ⁻	0.04 - 4	0.9999
Br ⁻	0.04 - 4	1.0000
NO ₃ ⁻	0.04 - 4	1.0000
PO ₄ ³⁻	0.1 - 10	0.9999
SO ₄ ²⁻	0.04 - 4	1.0000
NO ₂ (UV-VIS)	0.02 - 4	1.0000
Br ⁻ (UV-VIS)	0.02 - 4	0.9999
NO ₃ ⁻ (UV-VIS)	0.02 - 4	1.0000
Li ⁺	0.005-0.5	1.0000
Na ⁺	0.02 - 2	0.9999
NH ₄ ⁺	0.02 - 2	0.9999
K ⁺	0.05 - 5	0.9999
Mg ²⁺	0.05 - 5	0.9993
Ca ²⁺	0.05 - 5	0.9999

Applications

Fig. 4 to Fig. 7 show chromatograms of real samples. All analytical conditions are shown in Table 1.

Analysis of Mineral Water

Commercial mineral water (soft water) was analyzed after filtration with a 0.2 μm filter. Chromatograms are shown in Fig. 4.

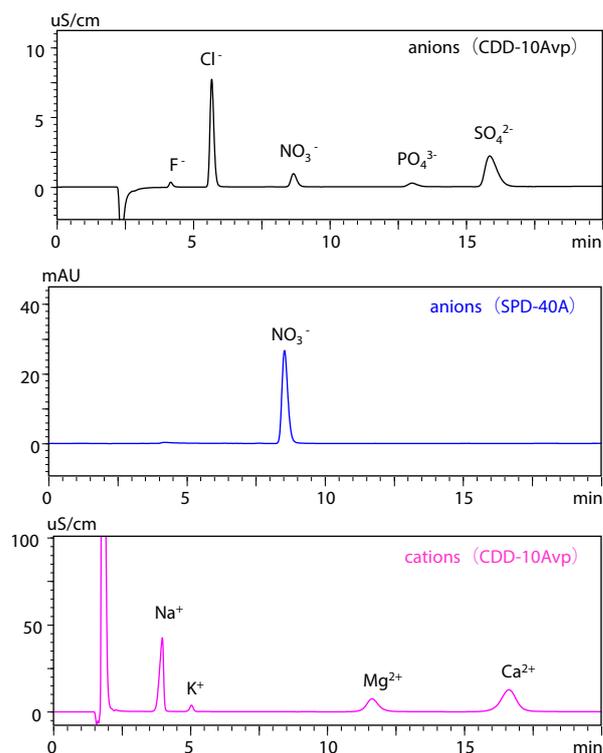


Fig. 4 Chromatograms of mineral water

● Analysis of River Water

River water was analyzed after filtration with a 0.2 μm filter followed by 20 times dilution with ultrapure water. Chromatograms are shown in Fig. 5.

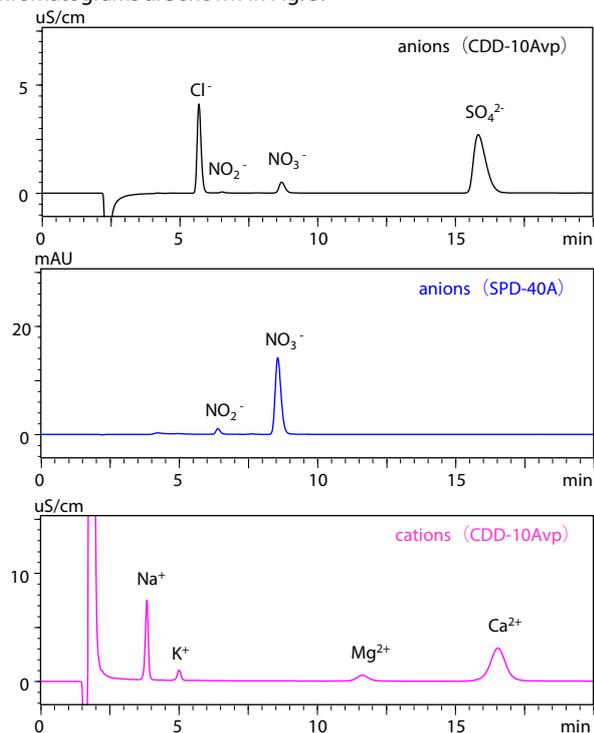


Fig. 5 Chromatograms of river water

● Analysis of Seawater

Seawater was analyzed after filtration with a 0.2 μm filter followed by 100 times dilution with ultrapure water. Chromatograms are shown in Fig. 6.

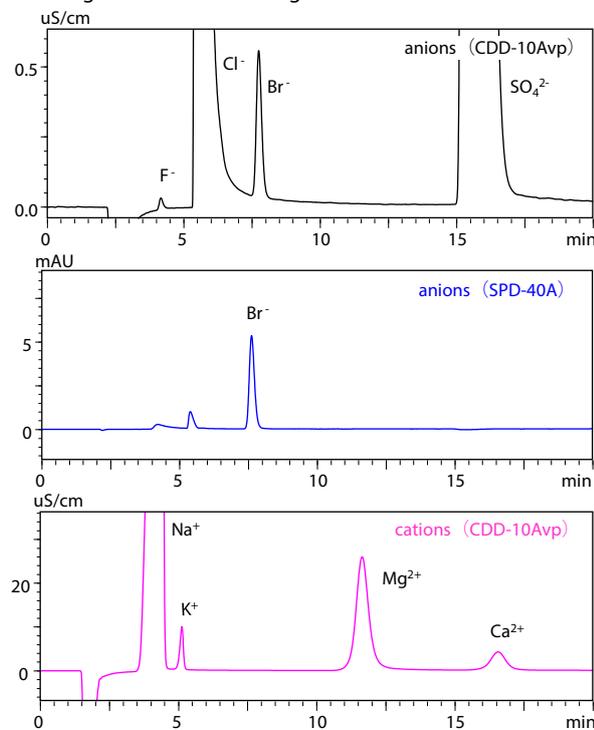


Fig. 6 Chromatograms of Seawater

● Analysis of Soil Extracted Water

The collected soil was shaken with ultrapure water, and centrifuged. The supernatant was analyzed after filtration with a 0.2 μm filter. Chromatograms are shown in Fig. 7.

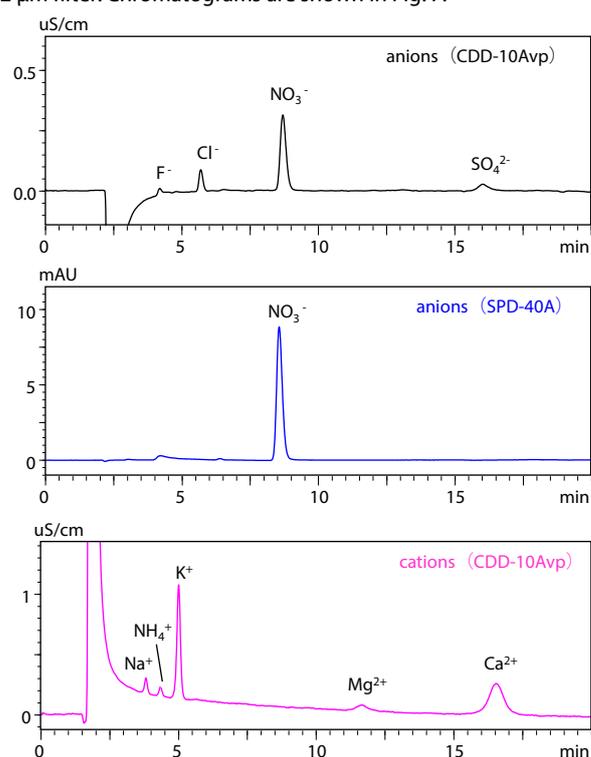


Fig. 7 Chromatograms of Soil Extracted Water

■ Conclusion

The ion chromatograph dual channel system and its applications are introduced in this article. By using this system, both anion and cation analytical results were obtained in a single run. In addition, by adopting a loop injection method for sample injection, good repeatability was obtained and cross-contamination was reduced. Preparation for starting analysis and cleaning after analysis can also be done in both flow channels at the same time, resulting in improved work efficiency.

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