Application News

No. L577

Ion Chromatography

Analysis of Cyanide Ion and Cyanogen Chloride in Mineral Water by Ion Chromatograph-Post Column Method

Mineral water has become an indispensable beverage in our daily lives, as annual per-capita consumption of mineral water in 2019 was 31.7 liters in Japan, 119 liters in the United States, 125.2 liters in Germany, and 147.4 liters in France [1].

Mineral water is classified as a soft drink, and safe products are distribution to the market based on compositional standards in Japan. In a revision of the standards for soft drinks and similar products, Ministry of Health, Labour and Welfare (MHLW) issued notification *Shokuan* 1222 No. 1 "Partial amendment to the Specifications and Standards for Foods, Food Additives, *Etc.* and the Ministerial Ordinance on Milk and Milk Products Concerning Compositional Standards, *Etc.*" dated December 22, 2014 [2], which set the content of cyanide ion and cyanogen chloride in mineral water at no more than a total of 0.01 mg/L, whether sterilized/disinfected or not. The CODEX international standard [3] for foods stipulates that the content of cyanide must not exceed 0.07 mg/L.

This article introduces an example of analysis of the cyanide ion and cyanogen chloride in three types of mineral water using a Shimadzu Nexera™ cyanic analysis system. The analysis complied with the Soft Drinks Test Method in MHLW notification *Shokuan* 1222 No. 4 (hereinafter, notification of enforcement) [4].

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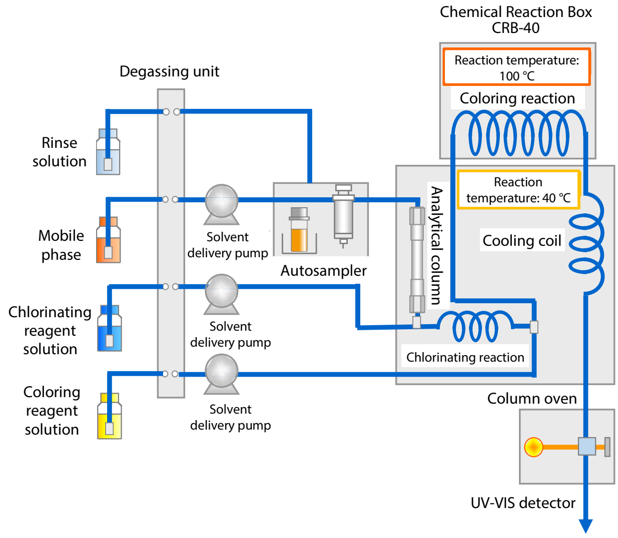

Fig. 1 Flow Channel Diagram

Analysis Method

In this analysis, detection is conducted at the wavelength of 638 nm using post-column derivatization by the 4-pyridinecarboxylate-pyrazolone method after separation of the cyanide ion and cyanogen chloride by the ion exclusion mode, in which a sodium tartrate buffer solution was used as the mobile phase. A two-stage reaction is used in this post-column method. The first reaction is a chlorination reaction with a chloramine T solution, and the second reaction is a coloring reaction using a 1-phenyl-3-methyl-5-pyrazolone/4-pyridinecarboxylate solution.

Fig. 1 shows the flow channel diagram of the Nexera cyanic analysis system compliant with the notification of enforcement. Table 1 shows the analysis conditions. To prevent cyanogen chloride from evaporating, the autosampler vials were cooled to 4 °C in this analysis.

Table 1 Analysis Conditions

<Separation>	
Column	: Shim-pack™ Amino-Na (100 mm×6.0 mm I.D., 5 µm) *1
Guard column	: Shim-pack CN(G) (10 mm×6.0 mm I.D., 5 µm) *2
Mobile phase	: 10 mmol/L Sodium tartrate buffer
Flow rate	: 0.6 mL/min
Column temp.	: 40 °C
Injection vol.	: 100 µL
Vial	: Shimadzu Vials, LC, Polypropylene *3
<Post-column reaction>	
First reaction	
Reagent	: Phosphate buffer containing 1 g/L Chloramine T
Flow rate	: 0.5 mL/min
Reaction temp.	: 40 °C
Second reaction	
Reagent	: 28.7 mmol/L 1-Phenyl-3-Methyl-5-Pyrazolone +96.5 mmol/L Sodium 4-Pyridinecarboxylate
Flow rate	: 0.5 mL/min
Reaction temp.	: 100 °C
Detection	: UV-VIS detector at 638 nm (Lamp: W)

*1 : P/N 228-18837-91, *2 : P/N 228-18837-93, *3 : P/N 228-31537-91

Analysis of Standard Solution

Fig. 2 shows the result when 100 µL of a standard solution of the cyanide ion and cyanogen chloride (0.01 mg/L each) was injected. The notification of enforcement requires separate preparation of the cyanide ion standard solution and the cyanogen chloride standard solution.

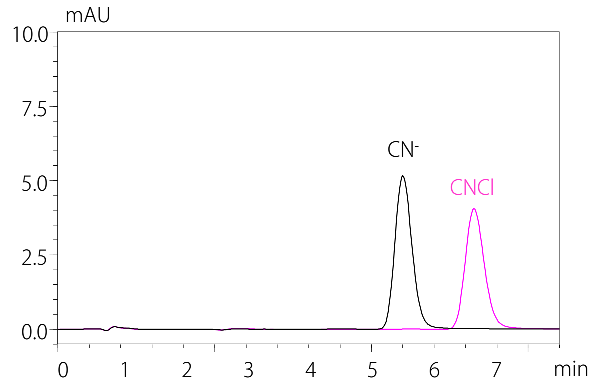

Fig. 2 Chromatogram of Standard Solutions of Cyanide Ion and Cyanogen Chloride (0.01 mg/L each)

Linearity of Calibration Curve

Fig. 3 shows the calibration curves of the cyanide ion and cyanogen chloride standard solutions. The calibration curves were prepared for the concentration range of 0.0025 to 0.025 mg/L, as specified in the notification of enforcement. The calibration curves showed good linearity, as the coefficient of determination (r^2) was 0.999 or higher.

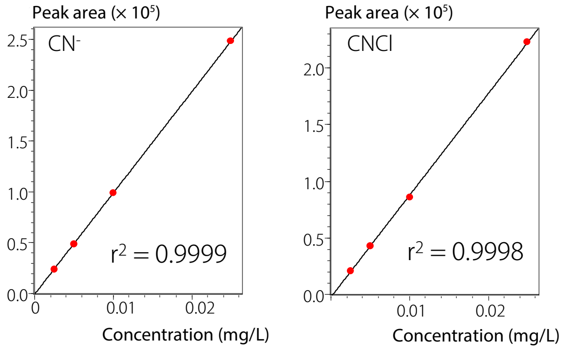

Fig. 3 Calibration Curves
(Left: Cyanide Ion, Right: Cyanogen Chloride)

Repeatability

Using 0.0025 mg/L of the standard solutions of the cyanide ion and cyanogen chloride, 6 continuous analyses were carried out, and the repeatability (peak area) of repeated injections was verified. The relative standard deviations of the cyanide ion and cyanogen chloride were 0.26% and 0.55%, respectively, showing satisfactory repeatability. Thus, it was found that system performance is stable.

Analysis of Mineral Water Samples

Figs. 4 to 6 show the results when 100 µL of three types of mineral water having different hardnesses was injected. The notification of enforcement does not allow addition of a phosphate buffer, as is done in analyses of tap water. The figures also show the results when 0.001 mg/L of the cyanide ion, i.e., 1/10 of the concentration of the standard value, was added to the mineral water. Fig. 7 shows the chromatograms of the 0.001 mg/L standard solution of the cyanide ion and ultrapure water. Table 2 shows the results of a spike-and-recovery test (Average of n = 3 each).

Table 2 Hardness and Recovery Rate of Mineral Water Samples

Name	Hardness [mg/L]	Recovery rate [%]
Mineral water A	10	102
Mineral water B	304	97
Mineral water C	1468	99

Conclusion

This article introduced an example of analysis of the cyanide ion and cyanogen chloride in three types of mineral water using a Shimadzu Nexera cyanic analysis system. The recovery rate was confirmed by adding the cyanide ion at a concentration of 1/10 of the standard value to the mineral water samples. Satisfactory recovery rates were obtained even with mineral waters having different hardnesses.

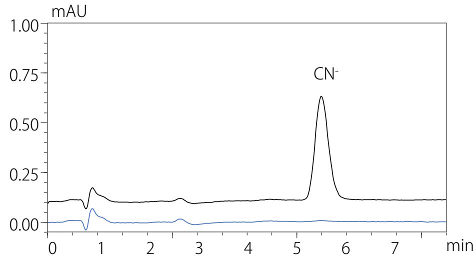

Fig. 4 Chromatogram of Mineral Water A
(Top: Mineral Water A with Addition of 0.001 mg/L of Cyanide Ion, Bottom: Mineral Water A)

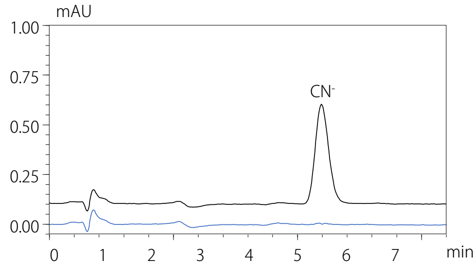

Fig. 5 Chromatogram of Mineral Water B
(Top: Mineral Water B with Addition of 0.001 mg/L of Cyanide Ion, Bottom: Mineral Water B)

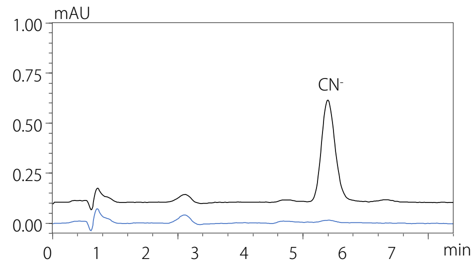

Fig. 6 Chromatogram of Mineral Water C
(Top: Mineral Water C with Addition of 0.001 mg/L of Cyanide Ion, Bottom: Mineral Water C)

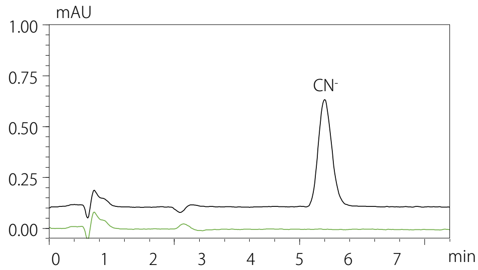

Fig. 7 Chromatogram of Standard Solution
(Top: 0.001 mg/L Standard Solution of Cyanide Ion, Bottom: Ultrapure Water)

<References>
(1) Statistical data of the Mineral Water Association of Japan, Transition of Per-Capita Consumption of Mineral Water (April 2, 2020) https://minekyo.net/relays/download/5/123/3/444/?file=/files/libs/444/202004021630262016.pdf (In Japanese only)
(2) Notification of the Ministry of Health, Labour and Welfare *Shokuan* 1222 No. 1, Partial amendment to the Specifications and Standards for Foods, Food Additives, *Etc.* and the Ministerial Ordinance on Milk and Milk Products Concerning Compositional Standards, *Etc.* dated December 22, 2014.
(3) CODEX Standard for Natural Mineral Waters: CXS 108-1981 (Adp. 1981, Rev. 1997, 2008, Amd. 2001, 2011, 2019)
(4) Notification of the Ministry of Health, Labour and Welfare *Shokuan* 1222 No. 4, Test Methods Related to Partial Amendment to Standards for Soft Drinks, *Etc.* dated December 22, 2014.

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