

Analysis of Cyanide Ion and Cyanogen Chloride by Post-column Ion Chromatography

On May 30, 2003, the Ministerial ordinance amendment related to the Japanese water quality standard was promulgated (Ministerial Ordinance Number 101; April 1, 2004 enforcement), and on July 22, 2003, the test methods were announced (Japanese Ministry of Health, Labor and Welfare Notification Number 261)*.

In this latest amendment, post-column ion chromatography was designated as the test method for the cyanide. The water quality criteria level for cyanide has been fixed at 0.01mg/L, which represents

the total for the cyanide ion and cyanogen chloride. For the analytical instrument to be used for performing this analysis, precision within 10% CV is required, using 1/10 the concentration of this criteria level, or 0.001mg/L(1 μ g/L), with an injection volume of 50 – 250 μ L.

Introduced here is an analysis example of the determination of the cyanide ion and cyanogen chloride using the Shimadzu LC-VP Cyanide Analysis System, which completely conforms to the new water test method.

*Partial amendment on March 30,2006 (Japan's Ministry of Health, Labour and Welfare Notification No.191)

■ Analytical Method

In the designated method, after separating the cyanide ion and cyanogen chloride using an ion replacement column, post-column derivatization by the 4-pyridinecarboxylic acid - pyrazolone method is performed, and detection is carried out at 638 nm. This post-column method performs a 2-stage reaction. In the first-stage reaction, chloramine-T is used, and in the second stage, a 1-phenyl-3-methyl-5-pyrazolone/4- pyridinecarboxylic acid solution is used. Fig. 1 shows a flow diagram of the LC-VP Cyanide analysis system, conforming to the designated test method.

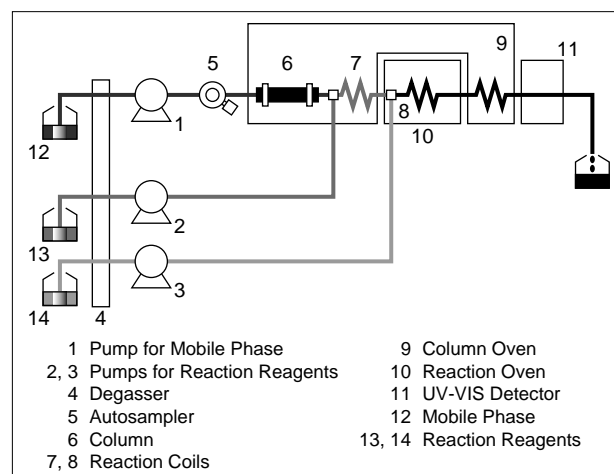


Fig.1 Flow Diagram

■ Analysis of Standard Solution

Fig. 2 shows the analysis result of the cyanide ion and cyanogen chloride (each 10 μ g/L) solutions, using 100 μ L injections. The analytical conditions are shown in Table 1.

As cyanide ion and cyanogen chloride are unstable,

they should be used immediately after being prepared. Especially, cyanogen chloride disappears even during analysis. To prevent this, autosampler vials should be cooled.

Table 1 Analytical Conditions

<Separation>	
Column	: Shim-pack Amino-Na (100mmL. \times 6.0mmI.D.)
Mobile Phase	: 10mM Tartrate (Na) Buffer (pH=4.2)
Flow Rate	: 0.6mL/min.
Column Temp.	: 40°C
<Post-column Reaction>	
First Reaction :	
Reagent	: 100mM Phosphate buffer Containing 1.8mM Chloramine T
Flow Rate	: 0.5mL/min.
Reaction Temp.	: 40°C
Second Reaction	
Reagent	: 14.4mM 1-Phenyl-3-Methyl-5-Pyrazolone +48.3mM 4-Pyridinecarboxylate (Na)
Flow Rate	: 0.5mL/min.
Reaction Temp.	: 100°C
Detection	: SPD-10AV _{VP} at 638nm

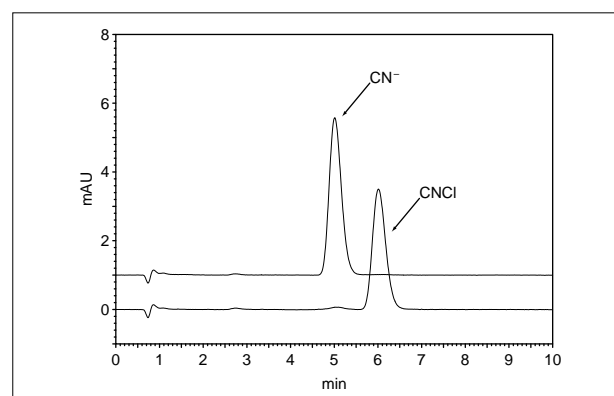


Fig.2 Chromatogram of Standard Cyanide Ion and Cyanogen Chloride (0.01mg/L each)

■ Repeatability and Linearity

Fig. 3 shows the repeatability (peak area and retention time) for each of the 1 μ g/L standard solutions with an injection volume of 100 μ L. At 1/10 the criteria level of 0.01mg/L, good repeatability is obtained.

Fig. 4 shows the calibration curves in the concentration range of 0.5 – 100 μ g/L. Good linearity is obtained.

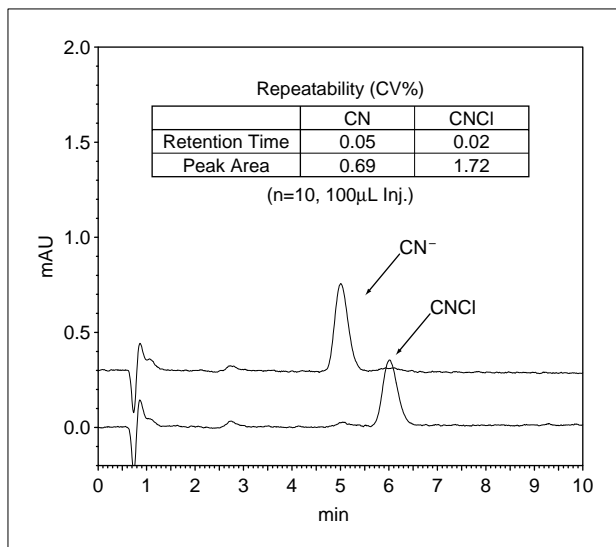


Fig.3 Repeatability of Standard Cyanide Ion and Cyanogen Chloride (1 μ g/L each)

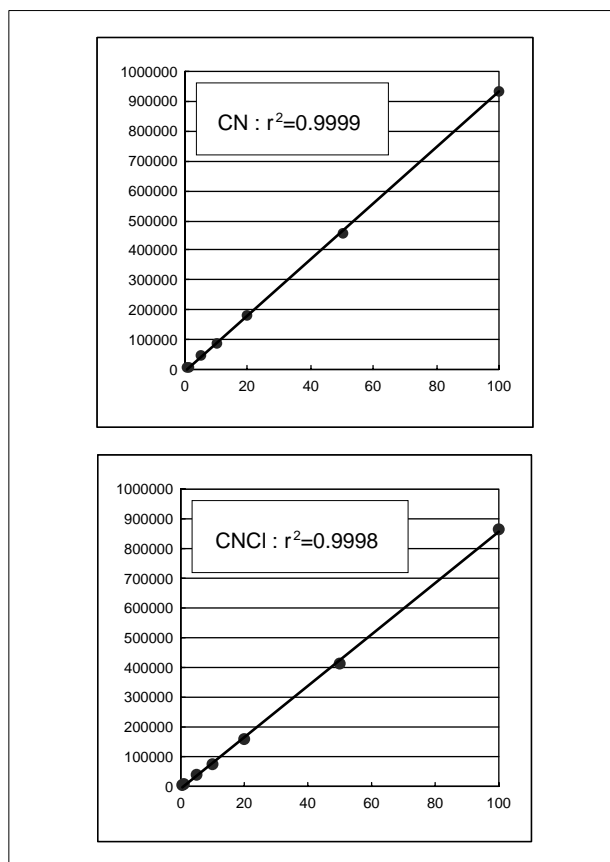


Fig.4 Calibration Curve (0.5–100 μ g/L)
(Upper : Cyanide, Lower : Cyanogen Chloride)

■ Analysis of Tap Water

Fig. 5 shows the analysis result based on a 100 μ L injection of tap water. The sample was injected after preparation in which tartaric acid solution and sodium tartrate buffer solution were added.

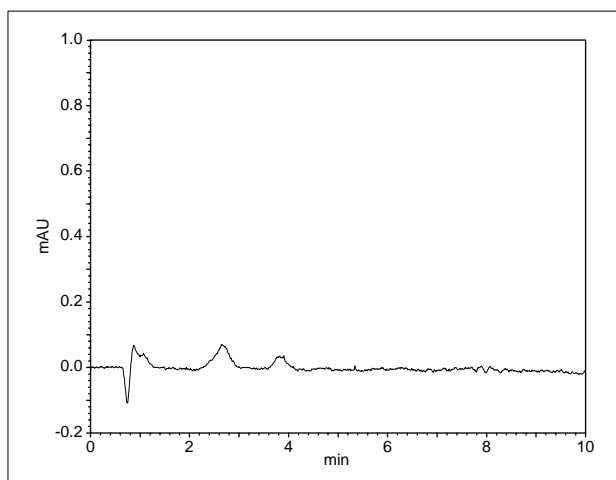


Fig.5 Chromatogram of Tap Water

Fig. 6 shows a chromatogram of this tap water to which the cyanide ions were added to bring the concentration to 1 μ g/L. Due to the effect of the residual chlorine in the tap water, almost all of the cyanide ions were converted to and detected as cyanogens chloride.

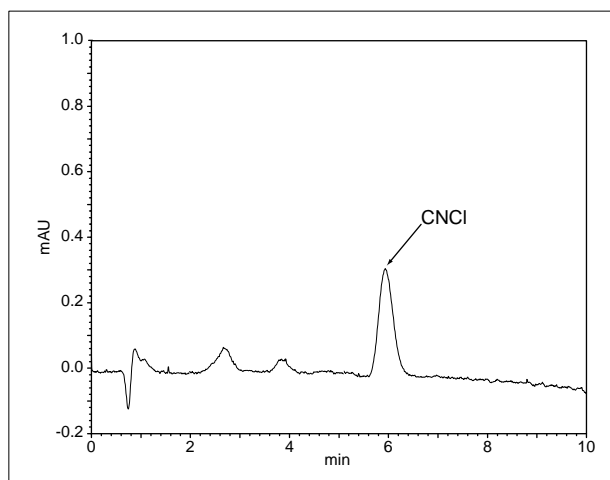


Fig.6 Chromatogram of Tap Water (Cyanide Ion 1 μ g/L spiked)