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Ion chromatography (IC) is a suitable analytical technique for the determination of anions. The cyanide is not detected by the conductivity detector of the ion chromatograph due to its low dissociation constant (pK = 9.2). This paper describes an IC procedure for the determination of free cyanide and metal cyanide complexes that uses a conductivity detector. It is based on the oxidation of cyanide ion by sodium hypochlorite to cyanate ion (pK = 3.66). Therefore, cyanide ion can now be measured indirectly by the conductivity detector. In this procedure, optimum operating conditions were examined. In addition, the interferences from anions and reducing agents were investigated. The method was applied to the determination of metal cyanide complexes. The coefficients of variation (%) for CN^- (1.05 mg/L), $Zn(CN)_4^{2-}$ (CN^-, 0.80 mg/L), and $Ni(CN)_4^{2-}$ (CN^-, 0.96 mg/L) were 1.1%, 1.5%, and 0.5%, respectively. The proposed method proved to be useful for the determination of cyanide compounds in natural water and wastewater.

Many methods have been developed for the determination of cyanide compounds in water, wastewater (*1*, *2*), and plating solutions (*3*). These methods make use of titrimetry, colorimetry, cyanide-selective electrodes (*1*, *2*), coulometry (*4*, *5*), gas chromatography (*6*), high-performance liquid chromatography (*7*), and so on.

Usually, ion chromatography (IC) is the most suitable technique for the separation and determination of both anions and cations (*8*). However, hydrogen cyanide cannot be directly detected by the conductivity detector of the ion chromatograph due to its low dissociation constant (pK = 9.2).

Girard reported the use of controlled potential coulometry as a detection method for cyanide ion (*9*). An IC with an amperometric detector was also used for the cyanide and/or metal cyanide determination by Bond et al. (*10*) and Rocklin et al. (*11*). Wang et al. reported a potentiometric measurement obtained by using an ion-selective electrode for the determination of cyanide and sulfide (*12*). These electrochemical methods are sensitive and selective for cyanide ion, but such detectors are too expensive and not familiar.

Another IC method without an electrochemical detector (ECD) has also been reported. Pinschmidt developed a procedure for the determination of weak acid ions including cyanide ion (*13*). Dolzine et al. proposed a procedure for the determination of hydrogen cyanide in air by converting it to sodium formate followed by its measurement (*14*). DuVal et al. used the reaction between cyanide ion and iodine (*15*). However, these methods are time consuming and/or troublesome. Some metal cyanide complexes such as iron, gold, and cobalt can be measured using a MPIC-NS1 separator column with a conductivity detector (*16*). Silinger reported a method that uses sodium hypochlorite to oxidize free cyanide ion (CN^-) to cyanate ion (CNO^-) before chromatographic

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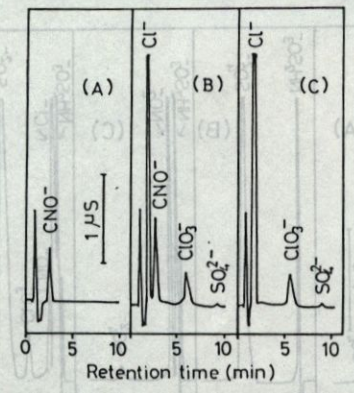

Figure 1. Chromatogram of cyanate ion: (A) CNO^- standard (pH 12); (B) CN^- (pH 12) 50 mL + NaClO (1%) 50 μL; (C) water (pH 12) 50 mL + NaClO (1%) 50 μL. Column, HPIC-AS4; eluent, 2.2 mM Na_2CO_3; detector, conductivity, full scale, 3 μS.

separation (*17*). However, the appropriate temperature, the stability of cyanate ion formed, the interferences, and the applicability to metal cyanide complexes have yet to be determined.

This paper describes an IC procedure for free cyanide and metal cyanide complex determination with a conductivity detector. This method is based on the oxidation of CN^- by sodium hypochlorite to CNO^-. This reaction is generally used physicochemically for wastewater treatment of cyanide compounds by alkaline chlorination (*1*) and also applies to the coulometric determination of cyanide ion (*4*, *5*). The stability constant of cyanate ion is low (pK = 3.66); therefore, it can be measured by a conventional conductivity detector. Various parameters such as the amount of sodium hypochlorite, temperature, stand time, and stability of the cyanate ion formed were optimized to provide quantitative conversion of CN^- to CNO^-. The interferences from anions and reducing agents and the applicability to the determination of the metal cyanide complexes were also investigated.

EXPERIMENTAL SECTION

Apparatus. Chromatography was performed on a Dionex system 2010i ion chromatograph equipped with a conductivity detector. The sample loop size was 50 μL. A separator column (HPIC-AS4 or HPIC-AS4A) with one guard column (HPIC-AG4) and a fiber suppressor (AFS-1) was used. The eluent was a solution of 2.2 mM Na_2CO_3. The eluent flow rate was 1.5 mL/min. The suppressor regenerant was 0.025 N H_2SO_4.

Reagents. All chemicals used were of the highest grade commercially available.

Standard cyanide solution was prepared from a 1000 mg of CN^-/L potassium cyanide stock solution, standardized by argentometric titration.

Standard metal cyanide complex solutions were prepared by accurate dilution of $KAg(CN)_2$, $K_2Ni(CN)_4$, $K_4Fe(CN)_6$, $K_3Fe(CN)_6$, $KAu(CN)_2$, $KAu(CN)_4$, and $K_3Co(CN)_6$ stock solution (1000 mg of CN^-/L). Solutions of $Zn(CN)_4^{2-}$, $Cd(CN)_4^{2-}$, and $Cu(CN)_4^{3-}$ were prepared by mixing KCN and the corresponding metal cyanide complexes ($Zn(CN)_2$, $Cd(CN)_2$, $KCu(CN)_2$) in appropriate amounts.

Procedure. In a volumetric flask (50 mL), place 5.0 mL of cyanide solution (10 mg/L, 10^{-2} N NaOH) and 4.5 mL of sodium hydroxide solution (10^{-1} N) and dilute to 50 mL with deionized water. Add 50 μL of sodium hypochlorite solution (1%) and mix thoroughly. Keep the mixture at a constant temperature between 20 and 80 °C for 10 min. The flask is cooled in a water bath and an aliquot is then injected into the ion chromatograph.

RESULTS AND DISCUSSION

Chromatogram of Cyanate Ion. Cyanate ion is detected by the conductivity detector because it is highly dissociative.

The chromatograms of cyanate ion from potassium cyanate and cyanate ion which is formed from cyanide ion and sodium hypochlorite solution are shown in Figure 1.

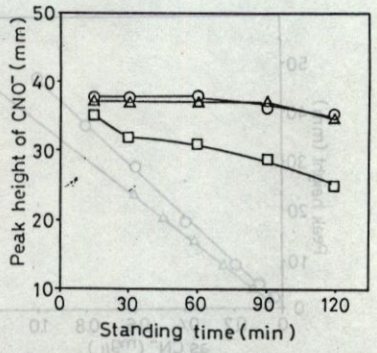

Figure 2. Stability of cyanate ion formed: CN^- solution (1 mg/L, 50 mL) pH 8.2 (□) 10.1 (△), and 11.7 (○). NaClO (1%), 50 μL; condition, 25 °C, 10 min stand; column, HPIC-AS4; eluent, 2.2 mM Na_2CO_3; detector, conductivity, full scale, 3 μS.

Both standard potassium cyanate (CNO^-, 1 mg/L) at pH 12 (A) and cyanate ion from cyanide ion (1 mg/L) at pH 12 (B) were analyzed by using 2.2 mM Na_2CO_3 eluent. This eluent is simpler than that of Silinger's (*17*). The chromatogram of a blank is shown in Figure 1C.

During the alkaline chlorination of cyanide at pH 12 by sodium hypochlorite, a positive peak, which is called the "pseudopeak", appeared. It is caused by an alkaline solution of the sample. The negative peak that appeared immediately after the pseudopeak is caused by the water formed in the suppressor. The positive peaks that followed are due to chloride, cyanate, chlorate, and sulfate ions (B). The retention times of these positive peaks are ca. 2.2, 2.7, 5.6, and 8.5 min, respectively.

Optimum Operating Condition for Cyanide Ion Determination. In order to determine the optimum amount of sodium hypochlorite for the conversion of CN^- to CNO^-, various amounts of sodium hypochlorite solution (1%) were added to the 50 mL cyanide solutions (1 mg/L, pH 12).

It was determined that 10 μL of sodium hypochlorite was insufficient to oxidize cyanide ion and resulted in a lower peak height. When 20–50 μL is used, the peak heights are almost constant. However, when over 60 μL is used, peak height is again lower. When the amount of sodium hypochlorite is increased, the chloride (Cl^-) peak is enlarged, and the separation of CNO^- from Cl^- becomes incomplete. Thereafter, the amount of sodium hypochlorite (1%) solution was fixed at 50 μL for the 50 mL of CN^- (1 mg/L) solution.

The effect of temperature on the conversion of CN^- to CNO^- was also examined. The peak heights of CNO^- formed are almost constant between 20 and 80 °C. The effect of stand time after addition of the sodium hypochlorite solution (1%) was checked at 25 °C. A stand time of 10–30 min does not make any difference. Therefore, the temperature was fixed at 25 °C (room temperature) and the stand time was fixed at 10 min for the free cyanide solution.

Stability of the Cyanate Ion Formed. The stability of formed cyanate ion was examined at the pH values, of the CN^- solutions, which were ca. 8, 10, and 12. The results are shown in Figure 2.

At pH 10 and 12, maximum peak heights were obtained within 15 min and were constant for about 60 min, but they did decrease after 90 min. On the other hand, peak height at pH 8 was lower than those at pH 10 and 12 and decreased after 30 min. It is theorized that CNO^- has an accelerated decomposition at pH 7–8 (*1*).

Calibration Curves. The calibration curves are shown in Figure 3. The first plot (25 °C) represents the cyanate ion standard, which is formed by the reaction of cyanide ion (pH 12) and sodium hypochlorite. The second plot represents the potassium cyanate standard.

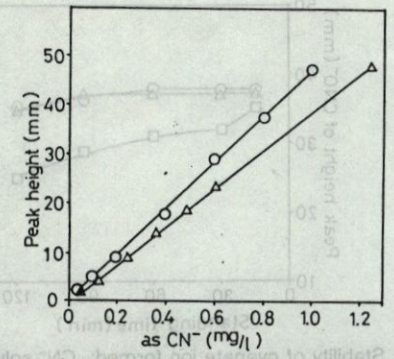

Figure 3. Calibration curves: (O) CN^- (pH 12) + NaClO, 25 °C, 10 min stand; (Δ) CNO^- (pH 12), 25 °C. Column, HPIC-AS4; eluent, 2.2 mM Na_2CO_3; detector: conductivity, full scale, 3 μS.

Table I. Interferences of Anions and Reducing Agents

anions and reducing agents	retention time, min	ppm ratio (CN^-/A^{n-})	recovery, %
F^-	1.6	1/10	98.3
Cl^-	2.2	1/10	97.4
Cl^-	2.2	1/100	85.7
NO_2^-	2.5	1/0.1	104.0
NO_2^-	2.5	1/1	>100.[a]
NO_2^-	2.5	1/10	>300.[a]
HPO_4^{2-}	4.3	1/10	98.3
Br^-	4.2	1/10	96.6
NO_3^-	4.8	1/10	98.3
SO_4^{2-}	8.5	1/10	93.2
S^{2-}		1/1	93.8
S^{2-}		1/10	0.8
SO_3^{2-}	4.5	1/1	100.0
SO_3^{2-}	4.5	1/10	102.0
$S_2O_3^{2-}$		1/1	103.0
$S_2O_3^{2-}$		1/10	47.4
PO_2^{3-}		1/1	96.9
PO_2^{3-}		1/10	93.8
PO_3^{3-}	3.3	1/1	98.4
PO_3^{3-}	3.3	1/10	78.9
$C_6H_8O_6$		1/1	100.0
$C_6H_8O_6$		1/10	76.3
AsO_2^-		1/1	98.4
AsO_2^-		1/10	103.0

[a] Separation is incomplete. CN^- solution (1 mg/L, pH 12), 50 mL; NaClO (1%) solution, 50 μL; condition, 25 °C, 10 min stand; column, HPIC-AS4; eluent, 2.2 mM Na_2CO_3; detector, conductivity, full scale, 3 μS.

The first plot at 25 °C was essentially a linear relationship between 0.05 and 1.0 mg/L cyanide ion. It indicated that the sodium hypochlorite–cyanide reaction is nearly stoichiometric.

The second plot also had a linear relationship between 0.06 and 1.24 mg/L cyanide ion. However, the slope of the potassium cyanate is slightly lower than that of the sodium hypochlorite–cyanide ion. The difference in slopes is thought to be due to the fact that high-purity potassium cyanate is not obtained and part of the cyanate decomposed.

Therefore, it is preferable that the calibration curve of cyanate is based on the reaction of standard cyanide ion (pH 12) and sodium hypochlorite solution.

Interferences. The effects of diverse anions and reducing agents on the cyanide analysis by the proposed method were examined. The results are shown in Table I.

The results indicate no interference from common anions such as fluoride, chloride, phosphate, bromide, nitrate, and sulfate ion. But, when chloride ion is increased, the separation of it from cyanate ion becomes incomplete. The retention time of nitrite ion (2.5 min) almost coincided with that of the cyanate ion (2.7 min). Therefore, a large amount of chloride

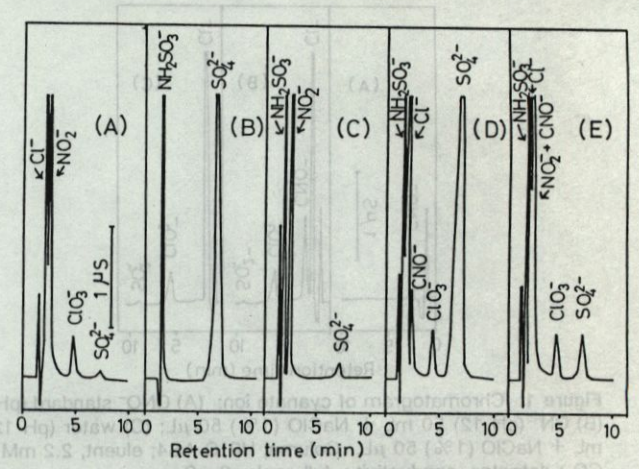

Figure 4. Decomposition or oxidation of nitrite ion: (A) NO_2^- (10 mg/L, pH 12) + NaClO; (B) NO_2^- (10 mg/L, pH 6.8) + NH_2SO_3H; (C) NO_2^- (10 mg/L, pH 12) + NH_2SO_3H; (D) {CN^- (1 mg/L) + NO_2^- (10 mg/L), pH 8} + NH_2SO_3H + NaClO; (E) {CN^- (1 mg/L) + NO_2^- (10 mg/L), pH 12} + NH_2SO_3H + NaClO; column, HPIC-AS4; eluent, 2.2 mM Na_2CO_3; detector, conductivity, full scale, 3 μS.

(100 mg/L) led to a negative error and a small amount of nitrite ion (more than 0.1 mg/L) led to a positive error.

When reducing agent is present in the sample, sodium hypochlorite is reduced. Larger amounts (10 mg/L) of reducing agent such as sulfide, thiosulfate, hypophosphite, phosphite, and ascorbic acid caused serious interference. But, a small amount (less than 1 mg/L) causes no interference. When larger amounts of reducing agent are present in a sample solution, an oxidation or distillation process is necessary as a pretreatment (*1*, *2*).

Decomposition of Nitrite Ion. The nitrite peak coincides with the cyanate peak. Therefore, when nitrite ion is present in a sample solution, suitable pretreatment is necessary for the removal of nitrite ion. It is recommended that amidosulfuric acid be used for the decomposition of the nitrite ion (*1*, *2*).

The oxidation of nitrite ion using sodium hypochlorite and the decomposition of nitrite ion using amidosulfuric acid were examined. The results are shown in Figure 4.

The nitrite ion (10 mg/L) at pH 12 was not oxidized to nitrate by sodium hypochlorite (A). The nitrite ion (10 mg/L) at pH 6.8 was decomposed by the amidosulfuric acid and produced sulfate ion (B). However, nitrite ion at pH 12 was not decomposed by the amidosulfuric acid (C).

In the next experiment, 0.5 mL of amidosulfuric acid solution (1%) was added to the mixed solution of cyanide and nitrite (pH 8), and allowed to stand for 10 min. Five milliliters of sodium hydroxide (0.1 N) was added and then diluted to 50 mL with water. Next, 50 μL of sodium hypochlorite (1%) was added and then allowed to stand for 10 min at 25 °C. The nitrite ion (pH 8) was decomposed and the cyanate peak clearly appeared (D). However, nitrite ion (pH 12) in the mixed solution ($CN^- + NO_2^-$) was not decomposed. Therefore, a large peak that was the sum of the cyanate and nitrite ions appeared (E).

The appropriate analytical procedures are as follows: (1) When nitrite ion is not present in a sample solution, add sodium hypochlorite at pH 12 without pretreatment and determine the cyanate ion. (2) When a small amount of nitrite ion is present, add amidosulfuric acid solution at pH 8 to decompose the nitrite ion. Then, add sodium hypochlorite at pH 12. (3) When a large amount of nitrite ion is present, nitrite ion can be decomposed by the amidosulfuric acid solution. Distillation is also required. Sodium hypochlorite is then added to the distillate (pH 12).

Analysis of Metal Cyanide Complexes. The cyanide compounds are present both as free and complexed cyanide.

Table II. Oxidation of Metal Cyanide Complexes by Sodium Hypochlorite

species	formation constant	20 °C	40 °C	60 °C	80 °C
$Zn(CN)_4^{2-}$	16.7	37.0[a]	36.5[a]	37.5[a]	36.5[a]
$Cd(CN)_4^{2-}$	18.8	39.0	38.0	38.5	39.0
$Cu(CN)_4^{3-}$	30.3	40.0	39.5	41.0	38.0
$Ag(CN)_2^-$	21.2	9.0	16.5	27.0	38.5
$Ni(CN)_4^{2-}$	31.3	9.0	33.5	40.0	41.0
$Fe(CN)_6^{4-}$	35	0.0	0.0	1.5	2.5
$Fe(CN)_6^{3-}$	42	0.0	0.0	0.0	0.0
$Au(CN)_2^-$	38.3	0.0	0.0	0.0	0.0
$Au(CN)_4^-$		0.0	0.0	2.0	7.0
$Co(CN)_6^{3-}$	64	0.0	0.0	0.0	0.0

[a] Peak height of CNO^- formed (mm). Metal complex (CN^-, ca. 1 mg/L, pH 12), 50 mL; NaClO (1%) solution, 50 μL; standing time, 10 min; column, HPIC-AS4; eluent, 2.2 mM Na_2CO_3; detector, conductivity, full scale, 3 μS.

Table III. Precision and Accuracy for Cyanide Compounds

cyanide compounds	CN^- (mg/L) mean[c]	SD	CV, %
CN^- (CN^-, 1.05 mg/L)[a]	1.00	0.011	1.1
$Zn(CN)_4^{2-}$ (CN^-, 0.80 mg/L)[b]	0.72	0.011	1.5
$Ni(CN)_4^{2-}$ (CN^-, 0.96 mg/L)[b]	0.90	0.004	0.5

[a] Measured by 4-pyridinecarboxylic acid–pyrazolone method. [b] Measured by 4-pyridinecarboxylic acid–pyrazolone method after the distillation for total cyanide of JIS[2]. [c] Measured by proposed method. Five samples at each concentration. CN^- and $Zn(CN)_4^{2-}$ were studied at 25 °C and $Ni(CN)_4^{2-}$ was studied at 80 °C after the addition of NaClO.

In order to study the chromatography of metal cyanides, solutions of zinc, cadmium, copper, silver, nickel, iron, gold, and cobalt cyanides were examined by the proposed method. The results are shown in Table II.

The results suggest that the complex cyanides can be grouped into three categories depending on the formation of cyanate ion by sodium hypochlorite and their cumulative formation constant.

Category 1 includes the weakly complexed and unstable cyanides such as $Zn(CN)_4^{2-}$, $Cd(CN)_4^{2-}$, and $Cu(CN)_4^{3-}$. These complexes could be analyzed after being oxidized with sodium hypochlorite to give cyanate ion. The peak height of the formed CNO^- was constant between 20 and 80 °C.

Category 2 includes the moderately strong cyanide complexes such as $Ag(CN)_2^-$ and $Ni(CN)_4^{2-}$. The cyanate peak height at 20 °C from these complexes is low. However, the peak height increases rapidly as the temperature increases. Maximum peak height was obtained at 60–80 °C.

Category 3 includes the strong cyanide complexes such as $Fe(CN)_6^{4-}$, $Fe(CN)_6^{3-}$, $Au(CN)_2^-$, $Au(CN)_4^-$, and $Co(CN)_6^{3-}$. These complexes are stable, therefore, almost no CNO^- peaks were detected even at 80 °C, except for $Fe(CN)_6^{4-}$ and $Au(CN)_4^-$.

Rocklin (*11*) also grouped the metal cyanide complexes into three categories and reported that $Zn(CN)_4^{2-}$ and $Cd(CN)_4^{2-}$ are quantitatively determined as total "free" cyanide, while $Cu(CN)_x^{n-}$ and $Ni(CN)_4^{2-}$ are only partially determined as "free" cyanide by ECD. Strong cyanide complexes were not detected by ECD.

Precision and Accuracy. The cyanide compounds such as CN^-, $Zn(CN)_4^{2-}$, and $Ni(CN)_4^{2-}$ were analyzed according to the proposed method. The results are shown in Table III.

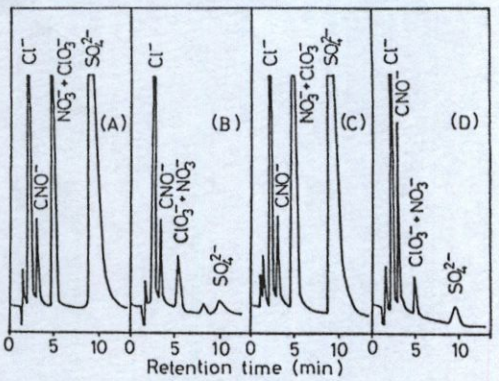

Figure 5. Cyanide analysis in water and wastewater: (A) drinking water spiked with 1.0 ppm cyanide ion; (B) groundwater spiked with 1.0 ppm cyanide ion; (C) river water (Nakagawa) spiked with 1.0 ppm cyanide ion; (D) plating wastewater (diluted to 50 times). Column, HPIC-AS4A; eluent, 2.2 mM Na_2CO_3; detector, conductivity, full scale, 3 μS.

The precision and accuracy of the proposed method on these compounds proved to be exceptionally good.

Application of the Proposed Method. The proposed method was applied to the analysis of cyanide ion in drinking water, groundwater, river water, and plating wastewater. A small amount of cyanide ion (50 μg) was added to 50 mL of sample solution except when using the plating wastewater. Plating wastewater was diluted 50 times with deionized water. In this experiment, a HPIC-AS4A separater column was used. The results are shown in Figure 5.

The cyanide compounds in all samples were analyzed indirectly by IC. Exceptionally good results were obtained. In the case when the HPIC-AS4A separater column was used, the retention times of chloride, cyanate, chlorate, and sulfate ions were ca. 2.5, 3.2, 5.3, and 9.8 min, respectively.

ACKNOWLEDGMENT

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Registry No. CN^-, 57-12-5; $Zn(CN)_4^{2-}$, 19440-55-2; $Ni(CN)_4^{2-}$, 48042-08-6; water, 7732-18-5.

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