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Indirect Determination of Cyanide Ion by Using Ion Chromatography with an Electric Conductivity Detector

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Abstract

Ion chromatography (IC) is the most useful analytical equipment for the determination of anions. The cyanide ion can not be determined by the electric conductivity detector of the IC due to its low dissociation constant ($pK = 9.2$). This paper describes an IC procedure for the determination of cyanide ion that uses an electric conductivity detector. The oxidation from cyanide ion to cyanate ion ($pK = 3.7$) was used by sodium hypochlorite with alkaline solution. Therefore, cyanide ion can be determined indirectly by using IC with an electric conductivity detector. In this study, optimum operating conditions and interferences from anions were examined. The method was applied to the determination of cyanide ion in environmental water samples.

The present approach was proved to be applicable for the determination of cyanide ion in river water and waste water.

Introduction

Cyanide compounds are used in electroplating factories of gold, silver, copper and cadmium; dressing plants, and the steel heat treatment industry. It is metal salt of hydrogen cyanide, and there is also sodium cyanide, potassium cyanide, zinc cyanide, copper cyanide, cadmium cyanide etc.. And there is the complex cyanide in which metal was combined with excess cyanide ion.

As for the cyanide compounds, there are substantially significant differences and forms of free cyanide ion in aqueous solution. Generally speaking, cyanide complex is water-soluble, but its complex ion is very stable. Accordingly, there is little toxicity.

The concentration of cyanide ion in environmental water samples is regulated strictly by its toxicity. The standard of CN^- in the Water Pollution Control Law is 1 mg/l ; the environmental standard is not detected. To manage drain, it is necessary to use a method that determines concentration of very

small amounts of cyanide ion.

Many methods have been developed for the determination of cyanide compounds in water, and waste water¹⁾, plating solutions²⁾. These methods make use of colorimetry, cyanide selective electrodes¹⁾, coulometry^{3,4)} and gas chromatography⁵⁾. The determination of cyanide ion using pyridine-*prazole* absorptiometry⁶⁾ is sensible, but there are problems such as conservation of solution or malodor of pyridine. And 4-pyridinecarboxal acid absorptiometry is different in coloring velocity by concentration.

As a means for determination of very small amounts of cyanide ion, the ion electrode method is used broadly. This method only replies to cyanide ion in cyanogen compound selectively. However, ions such as fluoride and chloride ion influence the determination of cyanide ion.

In cyanide ion analysis of sewer, it is necessary to separate hydrogen cyanide from cyanide compound.

In recent years the means by which very small amounts of cyanide ion are determined has been reported by the amperometry which combined ion chromatography with an electrochemical detector⁷⁾⁻¹⁰⁾. Ion chromatography (IC) is the most useful analytical method for the separation and determination of anions. However, hydrogen cyanide can not be directly determined by the electric conductivity detector of the IC due to its low dissociation constant ($pK = 9.2$).

This paper describes a determination method for cyanide ion using IC with an electric conductivity detector. This method is based on the oxidation of CN^- to CNO^- using sodium hypochlorite aqueous solution with alkaline solution.

The authors executed the investigation of the determination of cyanide ion by IC, which used electric conductivity detection to determine the presence of cyanide ion in environmental samples.

The authors introduced cyanate ion into IC after having been oxidized in cyanate ion using sodium hypochlorite aqueous solution with alkaline solution and examined the means by which cyanide ion of high sensitivity were determined by using electric conductivity detection. The present method makes it possible to determine cyanide ion at 0.05mg/l levels in environmental water samples.

Experimental

Apparatus and Regents

Determination of the Cyanide Ion by Using Electric Conductivity Detection

Figure 1 shows the apparatus of determination for the cyanide ion using IC. IC was used on Dionex 2010i equipped with an electric conductivity detector. The sample loop volume was $60\ \mu\text{l}$. A separator column (HPIC-AS4) with one guard column (HPIC-AG4) and a fiber suppressor (AFS-1) was used.

The eluant used sodium carbonate aqueous solution of 0.0010M . The eluant flow rate was 1.5 l/min . The suppressor regenerant was 0.0125M sulfuric acid.

Pure water was prepared by purifying distilled water with a Millipore Mili-Q SP system.

All chemicals used were an analytical reagent

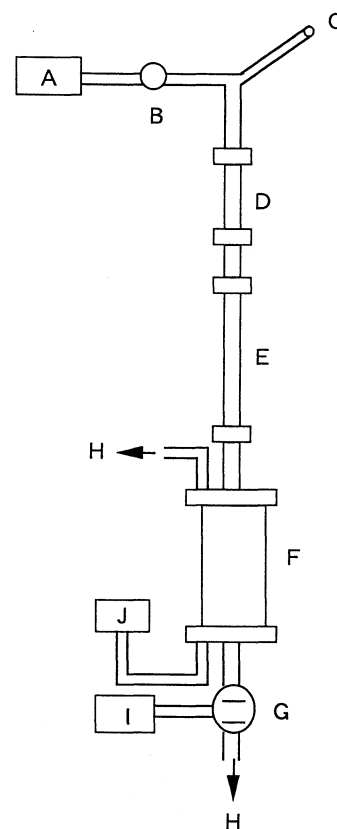


Fig. 1 Schematic diagram for determination of cyanide ion using ion chromatography with electric conductivity detector.

grade. Standard cyanide solution was prepared from a CN^- $1,000\text{ mg/l}$ potassium cyanide stock solution. Standard metal cyanide complex solutions were prepared by accurate dilution of $KAg(CN)_2$, $K_2Ni(CN)_4$, $K_2Cd(CN)_4$, $K_2Ni(CN)_4$, $K_2Zn(CN)_4$, $K_3Co(CN)_6$ and $K_3Fe(CN)_6$ stock solution (CN^- $1,000\text{ mg/l}$).

Procedure

In a volumetric flask (50 ml), add 5.0 ml of cyanide solution (10^{-2} M NaOH), 5.0 ml of sodium hydroxide solution (10^{-1} M) and $50\ \mu\text{l}$ of sodium hypochlorite solution (1%) and dilute to 50 ml with pure water. Then mix thoroughly and keep the mixture at a constant temperature in an oven for 10 min . The flask is cooled in a water bath and an aliquot is injected into the IC.

For the injection of the sample, a loop type injector of a capacity of $60\ \mu\text{l}$ is used.

The detector used electric conductivity detection

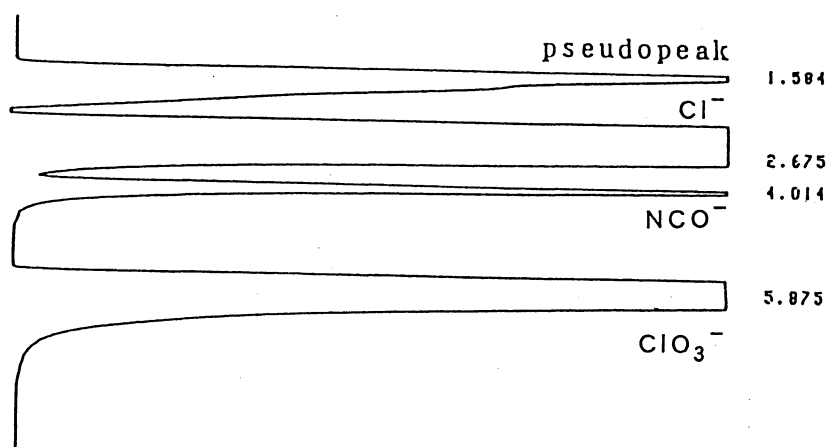


Fig. 2 Chromato pattern of cyanate ion : CN^- 1.00 mg/l (pH 12) 50ml + 1% NaClO 70 μ l.

and it combined data operation treatment apparatus and the peak area was converted to concentration.

The chromatography pattern of cyanate ion which is formed from cyanide ion with sodium hypochlorite solution is shown in Figure 2.

Figure 2 shows the chromatography pattern by IC, which used conductometric detection after CN^- 1.0 mg/l was oxidized with sodium hypochlorite aqueous solution. The cyanide ion is easily oxidized with sodium hypochlorite aqueous solution at pH levels of 10~12. The major chemical reaction of this time is as follows: cyanide ion is oxidized in cyanogen chloride with sodium hypochlorite aqueous solution on reaction (1). This reaction happens in a short amount of time.

The cyanogen chloride is a volatile substance which is toxic near to hydrogen cyanide gas.

Reaction (2) is the reaction in which cyanogen chloride form cyanate ion in an alkaline solution. This reaction occurs rapidly under strong alkaline conditions. Accordingly, cyanide ion does not generate cyanogen chloride when cyanate ion is oxidized with sodium hypochlorite aqueous solution in a strong alkaline solution. The authors examined oxidation conditions from the cyanide ion to cyanate ion using sodium hypochlorite aqueous solution.

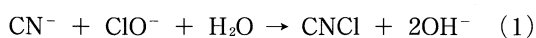


Figure 3 shows optimum operating conditions for cyanide ion determination.

The standard material of cyanide ion used was

potassium cyanide, and was prepared from a standard stock solution of cyanide ion 100 mg/l (10^{-2} M NaOH). Working solutions were prepared by diluting the stock solution with water.

Sample water introduces into sample loop from sample impregnation mouth of IC and goes through precolumn with eluant and enters two kinds of different columns connected continuously. Separation column used an OH^- type anion exchange resin of low capacity. Various ions are divided with separator column successively by affinity with resin, size of hydrated ion radius, mutual action of Van der Waals. Separated ions are introduced into removal column. Removal column is H^+ type and has a strong-acid cation exchanger.

Eluant was changed for aqua or carbonic acid of low electrical conductivity property and then electric conductivity of a baseline resulted in a lower peak height.

In the case when Sodium Carbonate Aqueous Solution is used as the eluant, cyanate ion is separated in separation column and its ion enters the electric conductivity cell. Electric conductivity obtained was converted to the peak area and its area was converted to concentration with data operation treatment apparatus automatically afterwards.

Results and Discussion

Chromatogram of Cyanate Ion

Cyanate ion is determined by the electric conductivity detector because it is highly dissociative.

The chromatogram of cyanate ion, which is formed from cyanide ion with sodium hypochlorite solution is shown in Figure 2.

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 (CN^- 1 mg/l, pH 12).

It was determined that 10 μl of sodium

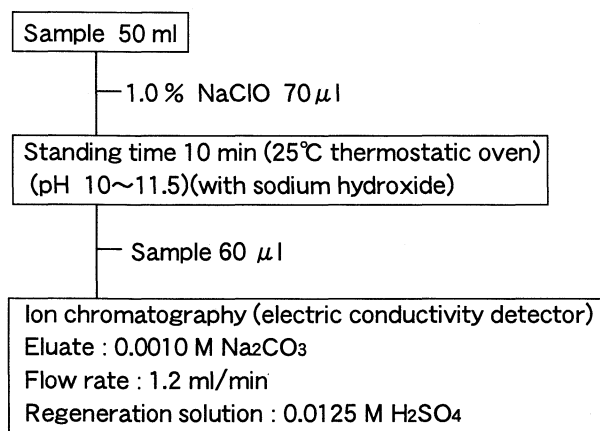


Fig. 3 Procedure for determination of cyanide ion using ion chromatography with an electric conductivity detector.

hypochlorite was insufficient to oxidize cyanide ion and resulted in a lower peak height. However, when over 60 μl is used, peak height is decreased again. When the amount of sodium hypochlorite is increased, the chloride ion peak is increased, and the separation of CNO^- and Cl^- becomes incomplete. Thereafter, the amount of sodium hypochlorite (1%) solution was fixed at 70 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 were almost constant between 25 and 50 $^{\circ}\text{C}$. The effect of stand time after addition of the sodium hypochlorite solution (1%) was checked at 25 $^{\circ}\text{C}$. The results do not differ with a stand time of 10~30 min. Therefore, the temperature was fixed at 25 $^{\circ}\text{C}$ and the stand time was fixed at 10 min for the free cyanide solution. Figure 3 shows the optimum operating conditions by the sodium hypochlorite oxidation method.

Calibration Curve

The calibration curve for cyanide ion determination is shown in Figure 4. This plot is a linear relationship between 0.05 and 1.0 mg/l cyanide ion. This method can be accurately determined the concentrations of the cyanide ion in the water samples.

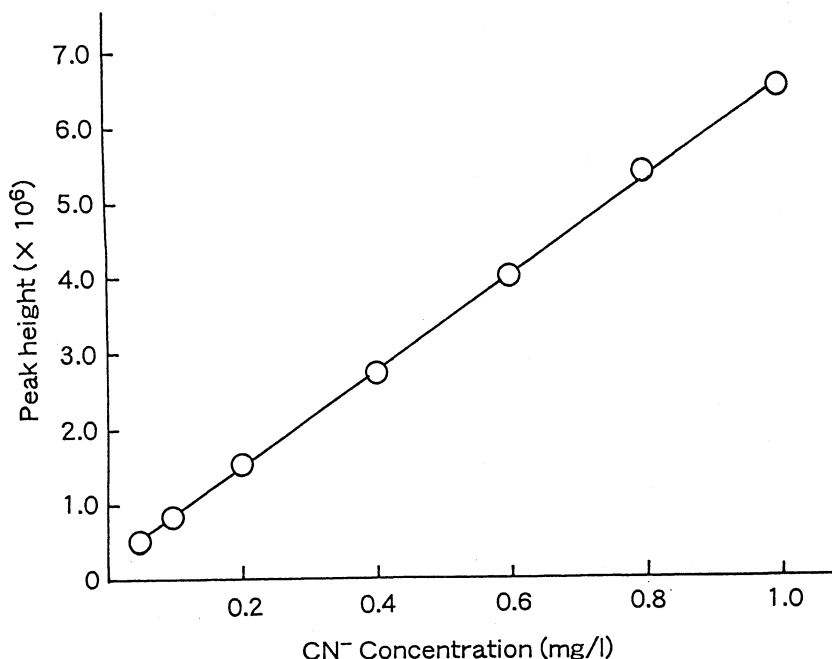


Fig. 4 Calibration curve for determination of cyanide ion using ion chromatography with an electric conductivity detector.

Precision

Table 1 shows reproducibility for standard cyanide solutions by using the sodium hypochlorite oxidation method with the optimum conditions. The table indicates that 0.05~1.0 mg/l of cyanide ion was determined three times by the present method. The detection limit (based on S/N = 2) was found to be about 0.02 mg/l. In repeated measurements of samples containing 0.10 and 0.60 mg/l of cyanide ion, the average value and the relative standard deviation were 0.099, 0.60₃ mg/l and 0.0032, 0.027, respectively.

Effect of Diverse Ions

Various ions are known to interfere with the determination of cyanide ion in environmental water samples.

The authors examined their influence on the determination of cyanide ion (CN⁻ 1.0 mg/l) containing fluoride ion, chloride ion, nitrite ion, bromide ion, nitrate ion, phosphate ion or sulfate ion. The result is shown in Table 2. Table 2 shows elution time and recovery of various ions. The fluoride ion, the

bromide ion, the phosphate ion and the sulfate ion are not clearly influenced from this table, but the peak of cyanate ion conflicts with the peak of chloride ion when the concentration exceeds 100 mg/l. Some removal countermeasures are necessary when chloride ion content exceeds 100 mg/l.

Removal of Coexistence Ions

The authors examined removal of interference of the chloride ion existing large amounts in environmental water samples.

1) Dilution Method

This method dilutes the concentration, which does not conflict with peak of thiocyanate and chloride ion. However this method cannot apply a low concentration of cyanide ion which includes a large quantity of chloride.

2) Pretreatment Method Using Silver Cartridge.

High capacity strong-acid cation exchanger of silver fills up this cartridge. This cartridge lets ions form precipitate of silver salt and can remove ion species such as chloride ion, bromide ion, iodide ion, arsenate ion, chromates ion and sulfide ion. But a part of silver salt of cyanate ion was deposited with this cartridge in addition to silver salt of chloride.

Metal Cyano Complex

The authors prepared aqueous solution of 1.0 mg/l as cyanogen using metal cyano complex (1) [Zn(CN)₄]²⁻, 2) [Cd(CN)₄]²⁻, 3) [Ag(CN)₂]⁻, 4) [Ni(CN)₄]²⁻, 5) [Fe(CN)₆]³⁻, 6) [Co(CN)₆]³⁻ and oxidation temperature and oxidation time was examined.

The results can be classified as follows;

- 1) [Zn(CN)₄]²⁻ and [Cd(CN)₄]²⁻ are easily oxidized to cyanide ion with sodium hypochlorite aqueous solution.
- 2) [Ag(CN)₂]⁻ and [Ni(CN)₄]²⁻ influence temperature of oxidation to cyanide ion with sodium hypochlorite aqueous solution.
- 3) [Fe(CN)₆]³⁻ and [Co(CN)₆]³⁻ can not be oxidized at 50 °C with sodium hypochlorite aqueous solution.

Application to Waste Water Samples

In order to examine the applicability to real samples, the present method was applied to the analysis of waste water samples. The analytical

Table 1 Reproducibility of cyanide ion determination

No.	Cyanide ion concentration (mg/l)						
	0.050	0.100	0.200	0.400	0.600	0.800	1.00
1	0.046	0.097	0.204	0.406	0.580	0.831	0.95 ₃
2	0.052	0.098	0.204	0.414	0.597	0.848	1.02
3	0.052	0.103	0.213	0.369	0.633	0.791	1.03
X _A	0.050	0.099	0.207	0.936	0.603	0.823	1.00

X_A : Arithmetic mean

Table 2 Effect of coexistence ions

Ion	Elution time (min)	Concentration ratio (CN ⁻ /A ⁿ⁻)	Recovery (%)
F ⁻	2.1	1/10	99.5
Cl ⁻	2.6	1/10	98.4
Cl ⁻	2.6	1/50	105
Cl ⁻	2.5	1/100	124
Cl ⁻	2.5	1/200	141
NO ₂ ⁻	3.5	1/0.1	97.4
NO ₂ ⁻	3.5	1/1.0	93.6
NO ₂ ⁻	3.5	1/10	170
Br ⁻	5.5	1/10	98.5
NO ₃ ⁻	6.4	1/10	97.8
SO ₄ ²⁻	18.6	1/100	102
HPO ₄ ²⁻	18.8	1/10	99.7

Table 3 Analytical results of cyanide ion in environmental water samples

Sample	CN-content (mg/l)
Drinking water	<0.05
Waste water of Kagoshima Univ. 1	<0.05
Waste water of Kagoshima Univ. 2	<0.05
Waste water of Kagoshima Univ. 3	<0.05
Waste water of Kagoshima Univ. 4	<0.05
Plating waste water 1	2.55
Plating waste water 2	<0.05
Plating waste water 3	<0.05

results are shown in Table 3. From the results so far described, cyanide ion was only determined from plating waste water samples.

The cyanide ion in environmental water samples was determined indirectly by using IC with an electric conductivity detector. This method was found to provide satisfactory results as a method to

determine trace amounts of cyanide ion in environmental water samples.

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