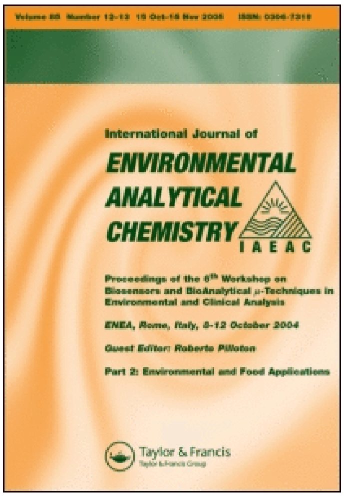

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Pretreatments for the Determination of Total Cyanide-Interferences, Effects of Reducing Agents and Additives

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PRETREATMENTS FOR THE DETERMINATION OF TOTAL CYANIDE—INTERFERENCES, EFFECTS OF REDUCING AGENTS AND ADDITIVES

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This paper describes some modifications of the JIS method for the determination of total cyanide. The interferences, effects of reducing agents and additives on the determination of total cyanide have been examined.

Hydrogen cyanide was formed during the distillation when using EDTA (JIS) in the presence of sodium nitrite, hydroxylammonium hydrochloride or hydrazonium dihydrochloride. It is preferable to use magnesium chloride and sulfuric acid instead of EDTA and orthophosphoric acid as additives and to use tin (II) chloride instead of L-ascorbic acid, sodium arsenite and sodium thiosulfate as reducing agents for the determination of total cyanide.

KEY WORDS: Total cyanide, pre-treatment, ISO, Standard Methods, JIS.

INTRODUCTION

Many standard methods have been issued for the determination of various forms of cyanide in water and wastewaters.[1]

As a preliminary treatment for the determination of total cyanide, Williams[2] proposed a distillation method after the addition of an acidic solution of cuprous chloride. The International Standard for Organization (ISO)[3] uses cupric sulfate, tin (II) chloride and hydrochloric acid. Serfass *et al.*[4] and Elly[5] reported a reflux method with magnesium chloride, mercuric chloride and sulfuric acid. The Standard Methods for the Examination of Water and Wastewater (American Public Health Association)[6] uses magnesium chloride and sulfuric acid. Kruse and Mellon[7,8] reported a distillation method with ethylenediaminetetraacetic acid disodium salt (EDTA) and citric acid in orthophosphoric acid solution. The Testing Method for Industrial Wastewater of Japanese Industrial Standard (JIS K0102)[9] uses EDTA, orthophosphoric acid and hydroxylammonium hydrochloride, which is used as a reducing agent. It has also been reported that hydrogen cyanide (HCN) is formed by the reaction of nitrogen-containing compounds and organic compounds.[10-17]

Previously, the author reported the effects of various organic compounds and nitrogen compounds on the formation of HCN and formation mechanism.[18] This paper describes interferences, and the effects of reducing agents and other additives for the determination of total cyanide. In addition, real samples were examined.

EXPERIMENTAL

Apparatus and Reagents

The same apparatus and reagents as previously reported were used,[18,21] except for the following reagents:

—The distillation apparatus designated by the JIS method[19] was employed for the determination of total cyanide.

—Magnesium chloride solution was prepared by dissolving 510 g of $MgCl_2 \cdot 6H_2O$ in 1 litre water.[6]

—Copper (II) sulfate solution (20% w/v) was prepared by dissolving 200 g of $CuSO_4 \cdot 5H_2O$ in 1 litre water. Tin (II) chloride solution (50% w/v) was prepared by dissolving 50 g of $SnCl_2.2H_2O$ in 40 ml of 1 M hydrochloric acid and then diluted with water to 100 ml.[3]

Deionized water was used throughout the experiment.

Procedure

The total cyanide determination procedure based on the JIS method[19] was used.

In order to investigate the effects of nitrogen compounds, 0.1 or 0.5 g of sodium nitrite, hydroxylammonium hydrochloride or hydrazonium dihydrochloride was added to a round-bottomed flask containing 150 ml of water. Additives such as EDTA, magnesium chloride or a mixed solution of copper sulfate and tin (II) chloride, and orthophosphoric acid were then added. The volume was made up to about 250 ml with water. The solution was immediately distilled into a 100-ml graduate cylinder which contained 20 ml of a 2% sodium hydroxide solution. About 70 ml of the solution were obtained by this distillation procedure. The resulting solution was diluted to 100 ml with water. Similarly, the effect of reducing agents, tin (II) chloride,[3] sodium thiosulfate[6] and ascorbic acid[9,20] was examined.

As for the effects of other additives, cuprous chloride and magnesium chloride were also examined. The additives, acids and reducing agents which were used in various standard methods[3,6,9,19,20] is presented in Table 1.

The cyanide ion in the distillate was determined by the pyridine-pyrazolone method.[19]

RESULTS AND DISCUSSION

Interferences in the Determination of Total Cyanide

Since various kinds of organic compounds are involved in the formation of

Table 1 Additives, acids and reducing agents for the separation of total cyanide

Methods	*ISO*	*Standard methods*	*JIS*
Sample	100 ml + H_2O 30 ml	250 ml	50 ml + H_2O 200 ml
Additives	$CuSO_4$ (20%) 10 ml $SnCl_2$ (50%) 2 ml	$MgCl_2$ (510 g/l) 10 ml	EDTA (10%) 10 ml
Acids	HCl 10 ml	H_2SO_4 (1:1) 25 ml	H_3PO_4 10 ml
Reducing agents	$SnCl_2$[a]	Na_2SO_3[b] $C_6H_8O_6$[c] $Na_2S_2O_3$[d,e] $NaAsO_2$[e]	Na_2SO_3[f] NH_2OHHCl[g] $NaAsO_2$[g,h] $C_6H_8O_6$[h]

[a] 1984; [b] 1971 (13th Ed.); [c] 1975 (14th Ed.); [d] 1980 (15th Ed.); [e] 1985 (16th Ed.); [f] 1971; [g] 1981; [h] 1986.

Table 2 Interferences of sodium nitrile

Interference		$NH_2SO_3NH_4$ (*g*)	*Additives*		*HCN formed*[a] (*μg*)
Species	*Amount* (*g*)		*Species*	*Amount* (*g*)	
$NaNO_2$	0.1		EDTA	1.0[b]	142
	0.5		EDTA	1.0	380
	0.1	0.3	EDTA	1.0	0.4
	0.5	1.5	EDTA	1.0	0.7
	0.1		$MgCl_2$	5.1[c]	0.8[e]
	0.5		$MgCl_2$	5.1	0.3[e]
	0.1	0.3	$MgCl_2$	5.1	0.0
	0.5	1.5	$MgCl_2$	5.1	0.0
	0.1		$CuSO_4 + SnCl_2$	2 + 1[d]	0.5[e]
	0.5		$CuSO_4 + SnCl_2$	2 + 1	0.2[e]
	0.1	0.3	$CuSO_4 + SnCl_2$	2 + 1	0.0
	0.5	1.5	$CuSO_4 + SnCl_2$	2 + 1	0.0

[a] In 100 ml. Blank value was subtracted.

[b] Recommended amount in JIS method.

[c] Recommended amount in Standard Methods.

[d] Recommended amount in ISO method.

[e] No_2 is detected.

HCN,[18] it is difficult to avoid the effect of organic compounds in wastewater. However, few nitrogen compounds form HCN.[18] Therefore, the effects and removal of nitrogen compounds such as sodium nitrite, hydroxylammonium hydrochloride and hydrazonium dihydrochloride were investigated. The results are presented in Tables 2 and 3.

Table 2 shows that sodium nitrite reacts with EDTA to form HCN. However, the amount of HCN significantly decreased when, in advance, nitrite ion was decomposed by ammonium amidosulfuric acid. Almost no HCN was formed from magnesium chloride or a mixed solution of copper sulfate and tin chloride when nitrite ion was decomposed.

Table 3 shows that hydroxylammonium hydrochloride and hydrazonium dihydrochloride react with EDTA to form HCN. In addition, the amount of HCN increased in the presence of potassium peroxodisulfate. However, almost no HCN was formed from hydroxylammonium hydrochloride and hydrazonium dihydro-

Table 3 Interferences of hydroxylammonium and hydrazonium salts

Interference		$K_2S_2O_8$ (g)	*Additives*		*HCN formed*[a] (μg)
Species	*Amount (g)*		*Species*	*Amount (g)*	
$NH_2OH \cdot HCl$	0.1		EDTA	1.0[b]	1.8
	0.5		EDTA	1.0	50.5
	0.1	0.27	EDTA	1.0	5460
	0.5	0.27	EDTA	1.0	6560
	0.1		$MgCl_2$	5.1[c]	0.0
	0.5		$MgCl_2$	5.1	0.1
	0.1	0.27	$MgCl_2$	5.1	0.0
	0.5	0.27	$MgCl_2$	5.1	0.0
	0.1		$CuSO_4 + SnCl_2$	2+1[d]	0.0
	0.5		$CuSO_4 + SnCl_2$	2+1	0.0
	0.1	0.27	$CuSO_4 + SnCl_2$	2+1	0.0
	0.5	0.27	$CuSO_4 + SnCl_2$	2+1	0.0
$N_2H_4 \cdot 2HCl$	0.1		EDTA	1.0[b]	0.2
	0.5		EDTA	1.0	0.8
	0.1	0.27	EDTA	1.0	164
	0.5	0.27	EDTA	1.0	180
	0.1		$MgCl_2$	5.1[c]	0.0
	0.5		$MgCl_2$	5.1	0.1
	0.1	0.27	$MgCl_2$	5.1	0.0
	0.5	0.27	$MgCl_2$	5.1	0.0
	0.1		$CuSO_4 + SnCl_2$	2+1[d]	0.0
	0.5		$CuSO_4 + SnCl_2$	2+1	0.0
	0.1	0.27	$CuSO_4 + SnCl_2$	2+1	0.0
	0.5	0.27	$CuSO_4 + SnCl_2$	2+1	0.0

[a] In 100 ml. Blank value was subtracted.
[b] Recommended amount in JIS method.
[c] Recommended amount in Standard Methods.
[d] Recommended amount in ISO method.

chloride when magnesium chloride or a mixed solution of copper sulfate and tin chloride were used. In this case, even in the presence of potassium peroxodisulfate, HCN was not formed.

Effects of Reducing Agents

Various kinds of reducing agents are employed in the standard methods,[3,6,9,19,20] which are presented in Table 1. In order to select a preferable reagent, the effects of reducing agents on the formation of HCN were examined. The results are presented in Table 4.

The results show that ascorbic acid produces HCN by the reaction with sodium nitrite or hydroxylammonium hydrochloride. When decomposing nitrite ion with ammonium amidosulfuric acid, the formation of HCN decreased. On the other hand, HCN was not formed in the reaction with tin (II) chloride and sodium nitrite or hydroxylammonium hydrochloride. In addition, almost no HCN was

Table 4 Effects of reducing agents

Interference		*$NH_2SO_3NH_4$ (g)*	*Reducing agent*		*HCN formed*[a] *(μg)*
Species	*Amount (g)*		*Species*	*Amount (g)*	
$NaNO_2$	0.1		$C_6H_8O_6$	0.1	16.4[b]
	0.5		$C_6H_8O_6$	0.1	54.4[b]
	0.1	0.3	$C_6H_8O_6$	0.1	6.8
	0.5	1.5	$C_6H_8O_6$	0.1	6.0
	0.1		$SnCl_2$	1.0	0.0[b]
	0.5		$SnCl_2$	1.0	0.0[b]
$NH_2OH \cdot HCl$	0.1		$C_6H_8O_6$	0.1	79.0
	0.5		$C_6H_8O_6$	0.1	116
	0.1		$SnCl_2$	1.0	0.0
	0.5		$SnCl_2$	1.0	0.0
$N_2H_4 \cdot 2HCl$	0.1		$C_6H_8O_6$	0.1	0.0
	0.5		$C_6H_8O_6$	0.1	0.0
	0.1		$SnCl_2$	1.0	0.0
	0.5		$SnCl_2$	1.0	0.0

[a] In 100 ml. Blank value was subtracted.
[b] NO_2 is detected.

formed in the reaction with hydrazonium dihydrochloride and ascorbic acid or tin (II) chloride.

Excess sodium thiosulfate[6] produced sulfite ion in sodium hydroxide absorbing solution during distillation. This interfered with the colour developing for the cyanide determination. Sodium arsenite is a poisonous reagent; therefore, it is not suitable.

On the basis of the results, it is recommended to use tin (II) chloride as the reducing agent.

Effects of Additives

A large amount of HCN was formed from EDTA, tartaric acid and citric acid.[18] In the JIS method,[9,19] the EDTA is used as an additive for the total cyanide determination. As additives, copper sulfate and tin (II) chloride are used in ISO[3] and magnesium chloride is used in Standard Methods[6] to decompose metal cyanide complexes. Therefore, copper sulfate, tin (II) chloride and hydrochloric acid, or magnesium chloride and sulfuric acid were used in the JIS method instead of EDTA and orthophosphoric acid. The results on the recovery of cyanide ion from metal cyanide complexes are presented in Table 5.

When cuprous ion or magnesium chloride were used, the recoveries of cyanide ion from $Ni(CN)_4^{2-}$, $Fe(CN)_6^{4-}$ and $Fe(CN)_6^{3-}$ were almost the same as when EDTA was used. The recoveries of cyanide ion from $Au(CN)_2^-$, $Au(CN)_4^-$ and $Co(CN)_6^{3-}$ were unsatisfactory, even though EDTA was added. However, the recovery of cyanide ion increased by using magnesium chloride or cuprous ion.

When magnesium chloride or cuprous ion was used, HCN was not formed, and

Table 5 Effects of additives on the recovery of cyanide from metal cyanide complexes

Cyanide complexes		*Average recovery (%)*[a]		
Species	*CN⁻ (μg)*	*EDTA*[b]	*MgCl$_2$*[c]	*CuSO$_4$+SnCl$_2$*[d]
$Ni(CN)_4^{2-}$	100.4	98.5	98.2	92.0
$Fe(CN)_6^{4-}$	100.1	97.9	98.5	96.8
$Fe(CN)_6^{3-}$	100.1	96.3	97.2	97.1
$Au(CN)_2^-$	100.2	11.1	53.2	55.7
$Au(CN)_4^-$	100.6	7.7	28.7	72.9
$Co(CN)_6^{3-}$	100.1	2.6	5.6	4.0

[a] Three samples at each concentration.
[b] Recommended in JIS method.
[c] Recommended in Standard Methods.
[d] Recommended in ISO method.

Table 6 Real sample analysis

Sample	*Interferences*	*Red/Ox agents*	*Additives (g)*		*CN⁻ found (mg/l)*
A	NO_2^-		EDTA	1.0	1.8
	NO_2^-		MgCl$_2$	5.1	1.0
	–[a]		EDTA	1.0	1.0
	–[a]		MgCl$_2$	5.1	0.6
B	$S_2O_8^{2-}$, Org.	NH$_2$OHHCl	EDTA	1.0	4.0
	$S_2O_8^{2-}$, Org.	NH$_2$OHHCl	MgCl$_2$	5.1	0.1
	$S_2O_8^{2-}$, Org.	$C_6H_8O_6$	EDTA	1.0	0.1
	$S_2O_8^{2-}$, Org.	$C_6H_8O_6$	MgCl$_2$	5.1	0.0
C-1	NH$_2$OH, EDTA SO_3^{2-}, $S_2O_3^{2-}$	KMnO$_4$			3.8[b]
C-2	NH$_2$OH, EDTA SO_3^{2-}, $S_2O_3^{2-}$	KMnO$_4$			0.1[b]

A: Wastewater of metal heat treatment.
B: Wastewater of printed circuit board plating.
C-1: Colour developing solution (new).
C-2: Waste solution of photographic processing.
[a] Decomposition with ammonium amidosulfuric acid.
[b] Oxidation with potassium permanganate, twice distilled.

the recovery of cyanide ion was increased over that of the EDTA results. However, when cuprous ion is used, high concentrations of copper waste have to be discarded. Therefore, it is recommended to use magnesium chloride instead of EDTA in the JIS method.

Optimized Analytical Procedure

The optimized analytical procedures for the determination of total cyanide are shown in Scheme 1.

When a reducing agent is present in a sample solution, it must be oxidized by

Scheme 1 Optimized analytical procedure

Sample taken (50–200 ml)
←Add $KMnO_4$ for reducing agent
or
←Add $SnCl_2$ for oxidizing agent
←Add $NH_4SO_3NH_2$ to decompose NO_2^- (at pH 6–8)
←Add water
250 ml
←Add 10 ml of $MgCl_2$ (510 g/l)
←Add 25 ml of H_2SO_4 (1:1)
Distillation
in 2% NaOH solution 20 ml
←Add water
Distillate (100 ml)
CN^- determination

potassium permanganate.[19] On the other hand, when an oxidizing agent is present, it should be reduced by tin (II) chloride. When nitrite ion is present in a sample solution, ammonium amidosulfuric acid should be added at pH 6–8.[21] Typically, 10 ml of 510 g/l magnesium chloride and 25 ml of (1:1) sulfuric acid were added to liberate hydrogen cyanide from the sample solution containing metal cyanide compounds, with subsequent distillation.

The determination of cyanide ion in sodium hydroxide solution will be performed by titrimetry, colorimetry, ion-selective electrode analysis or by ion chromatography.[21]

Real Sample Analysis

Real wastewaters contain various kinds of organic compounds and nitrogen compounds. Some samples which produce cyanide ion are shown in Table 6.

It is known that cyanide ion is formed in the wastewater of metal heat treatment.[22] It is formed by the reaction of nitrite ion and amines,[10,11] or nitrite ion and EDTA.[10]

The amount of cyanide ion from EDTA is larger than that when magnesium chloride is used. The cyanide amount produced decreased when decomposing nitrite ion with ammonium amidosulfuric acid.

As another example, cyanide ion was formed from a wastewater of the printed circuit board plating industry by adding hydroxylammonium hydrochloride and EDTA. However, almost no cyanide ion was formed when tin (II) chloride and magnesium chloride are used.

As further examples, colour developing and waste solutions of photographic processing were examined. Hydroxylammonium sulfate and various kinds of organic compounds such as EDTA, glycols, alcohols, acetic acid, aromatic amines (colour developing agent) are incorporated in these solutions.[23] The results showed that HCN was formed by the reaction of these reagents during distillation in the colour developing solution and a waste solution. False detection of cyanide ion, therefore, is often encountered in photographic processing solutions and waste solutions.

CONCLUSIONS

1) Nitrogen compounds such as hydroxylammonium salt, nitrite salt and hydrazonium salt interfere in the determination of total cyanide in the presence of organic compounds.
2) EDTA is used as an additive for the determination of total cyanide in the JIS method; however, it becomes the carbon source for HCN formation.
3) It is recommended to use magnesium chloride and sulfuric acid instead of EDTA and orthophosphoric acid.
4) L-Ascorbic acid, used as the reducing agent in the JIS method, also forms HCN in the presence of nitrogen compounds.
5) It is recommended to use tin (II) chloride as the reducing agent instead of L-ascorbic acid, sodium arsenite or sodium thiosulfate.

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