

# Endogenous Formation of Hydrogen Cyanide During Distillation for the Determination of Total Cyanide

MAKOTO NONOMURA

*Department of Chemistry, The Tokyo Metropolitan Industrial Technology Center, 13-10, Nishigaoka 3-Chome, Kita-ku, Tokyo 115, Japan*

*(Received 30 June 1987; in final form 3 October 1987)*

This paper describes how organic compounds and nitrogen compounds induce the formation of hydrogen cyanide during the distillation process. Hydrogen cyanide formation was confirmed by X-ray diffraction. The formation scheme for hydrogen cyanide from organic compounds is proposed.

**KEY WORDS:** Nitrogen compounds, hydrogen cyanide, organic compounds, X-ray diffraction.

## INTRODUCTION

For the determination of total cyanide in wastewater, distillation is the most commonly accepted means for sample pretreatment. Kruse and Mellon<sup>1,2</sup> recommended a distillation using ethylenediamine-tetraacetic acid disodium salt (EDTA) or citric acid in orthophosphoric acid solution. Ludzack *et al.*<sup>3</sup> reported another distillation method in which tartaric acid in acidic solution was used instead of EDTA. The Testing Method for Industrial Wastewater of Japanese Industrial Standard (JIS K0102) uses EDTA and orthophosphoric acid.<sup>4</sup>

As is mentioned in the JIS and the Standard methods (American Public Health Association), it should be remembered that hydrogen cyanide is formed during distillation by the reaction of nitrite ion with organic compounds.<sup>4,5</sup>

Koshimizu *et al.*<sup>6,7</sup> and Kanno *et al.*<sup>8,9</sup> reported that cyanide ion was formed when a mixture of aliphatic or aromatic amines and sodium nitrite was distilled in dilute sulfuric acid solution.

Owerbach also reported that formaldoxime, which was formed from formaldehyde and hydroxylammonium, was decomposed to produce hydrogen cyanide during distillation. These reagents are present in photographic processing effluents.<sup>10</sup>

Previously, the author reported that hydrogen cyanide was formed during distillation of wastewater samples from factories involved in printed circuit board plating.<sup>11,12</sup> As is recommended in JIS, the wastewater, which contained sodium peroxodisulfate, was distilled in the presence of hydroxylammonium hydrochloride, EDTA and orthophosphoric acid. The hydroxylammonium hydrochloride is used as reducing agent in JIS.<sup>4</sup>

The formation of hydrogen cyanide during distillation via the recommended method is not clearly understood and may produce erroneous results for total cyanide determination.

Therefore, in this paper, various kinds of organic compounds and nitrogen compounds were examined as to their effect on the formation of hydrogen cyanide in a similar distillation process. Results obtained showed that most organic compounds produced hydrogen cyanide. Some inorganic nitrogen compounds such as hydroxylammonium salt, sodium nitrite and hydrazonium dihydrochloride also produced hydrogen cyanide.

Hydrogen cyanide formation was confirmed by X-ray diffraction after absorption of the distilled vapor into silver nitrate solution. In addition, the formation scheme for hydrogen cyanide from the aforementioned organic compounds is proposed.

## EXPERIMENTAL

### Apparatus and reagents

The distillation equipment required by the JIS method<sup>4</sup> was employed for the determination of total cyanide.

For the determination of cyanide ion in the distillate, a Hitachi model 101 single-beam spectrophotometer with 10 mm cells was used.

The X-ray diffraction apparatus used for the identification of cyanide was a Rigaku-Denki D-10C X-ray diffractometer equipped with a copper-cathode X-ray tube.

In order to analyze the ions in the solution, a Dionex model 2010i ion chromatograph equipped with a conductivity detector was used. An HPICE-AS1 separator column and an ISC-ICE(Ag) suppressor column were used. The eluent was 2 m M hydrochloric acid.

All chemicals used were of the highest grade commercially available.

For the preparation of standard cyanide solutions, 2.51 g of potassium cyanide was dissolved in water and diluted to 1 l (1000 mg of  $\text{CN}^{-1}/\text{l}$ ). Working solutions were prepared by diluting the stock solution with water.

Buffer solution (pH 6.8) was prepared by dissolving 34.0 g of potassium dihydrogenphosphate and 35.6 g of disodium hydrogenphosphate in 1 l water.

Pyridine-pyrazolone reagent was obtained by dissolving 0.25 g of pyrazolone in 100 ml of hot water (75°C). After cooling, it was mixed with 20 ml of bis(pyrazolone) in pyridine (1 mg/ml). It was prepared daily.

Chloramine-T solution (1% w/v) was also prepared daily.

Deionized water was used throughout the experiment.

### Procedure

The total cyanide determination procedure is based on the JIS method.<sup>4</sup>

Briefly, in a round-bottom flask containing 150 ml of water, was added 1.0 m mol of potassium peroxodisulfate, hydroxylammonium hydrochloride and the organic test compound. After 10 ml of orthophosphoric acid was added, the volume was diluted to about 250 ml with water. The solution was immediately distilled into a 100 ml graduate cylinder which contained 20 ml of 2% sodium hydroxide aqueous solution. About 70 ml of product was obtained by this distillation procedure. The resulting solution was diluted to 100 ml with water.

Similarly, the formation of hydrogen cyanide from potassium peroxodisulfate, EDTA and nitrogen compounds were investigated.

The cyanide ion in the distillate was determined by the pyridine-pyrazolone method.<sup>4</sup>

In order to confirm cyanide formation, the distillate vapor was absorbed in silver nitrate solution (0.1 N). The resulting precipitate was filtered and dried under reduced pressure. An X-ray diffraction pattern of the precipitate confirmed the presence of cyanide.

## RESULTS AND DISCUSSION

### Effects of organic compounds on the formation of HCN.

First, formation of hydrogen cyanide was studied using organic compounds with or without a carbonyl group (1 mmol) in the presence of potassium peroxodisulfate (1 mmol) and hydroxylammonium hydrochloride (1 mmol). Results are shown in Tables 1 and 2, and blank value (av.  $0.59 \mu\text{mol}$ ) is subtracted.

As shown in Tables 1 and 2, hydrogen cyanide was formed not only from compounds with a carbonyl group such as carboxylic acids, aminocarboxylic acids, oxycarboxylic acids, aldehydes, ketones, and acidamides, but also from compounds without a carbonyl group such as aromatic hydrocarbons, alcohols, amines and pyridines.

The results suggest the following conclusions: Organic compounds with a carbonyl group produce hydrogen cyanide (Table 1). The only exceptions were sodium formate and oxalic acid which produced almost no hydrogen cyanide.

- 1) The amount of hydrogen cyanide becomes smaller with an increase in carbon number.
- 2) If a compound has a double bond, it produces a larger amount of hydrogen cyanide.
- 3) Carbonyl compounds containing an amino group or hydroxyl group produced larger amounts of hydrogen cyanide than carboxylic acids.
- 4) When the number of carboxylic, amino or hydroxyl groups was increased, more hydrogen cyanide resulted.

**Table 1** Relation between organic compounds containing carbonyl group and the amount of hydrogen cyanide formed<sup>a</sup>

Compounds (1 m mol)	HCN ( $\mu$ mol) <sup>b</sup>	Compounds (1 m mol)	HCN ( $\mu$ mol) <sup>b</sup>
<i>Carboxylic acids</i>		<i>Oxycarboxylic acids</i>	
Sodium formate	0.0	Hydroxyacetic acid	25.7
Sodium acetate	4.1	Lactic acid	4.5
Propionic acid	1.9	Sodium gluconate	55.2
<i>n</i> -hexanoic acid	0.0	Potassium sodium tartrate	39.0
Acrylic acid	5.5	Citric acid	13.2
Oxalic acid	0.3	Sodium salicylate	1.2
Succinic acid	6.5	Gallic acid	4.2
Adipic acid	0.3		
Maleic acid	16.2	<i>Aldehydes</i>	
Sodium benzoate	2.0	Acetaldehyde	16.3
Potassium biphthalate	2.1	Propionaldehyde	3.1
		Acrolein	17.5
		Benzaldehyde	1.0
<i>Aminocarboxylic acids</i>		<i>Ketones</i>	
Aminoacetic acid	9.2	Acetone	5.0
6-aminohexanoic acid	0.1	4-methyl-2-pentanone	6.5
L- $\alpha$ -alanine	1.6	Acetylacetone	4.2
L-aspartic acid	11.1		
L-glutamic acid	5.4	<i>Acidamides</i>	
L-lysine monohydrochloride	3.3	Acetamide	4.6
L-arginine monohydrochloride	5.0	N,N-dimethylformamide	3.1
Iminodiacetic acid	13.2	N,N-dimethylacetamide	2.6
Ethylenediaminediacetic acid	18.3	Acetanilide	0.3
Nitrilotriacetic acid	88.6		
Ethylenediaminetetraacetic acid	141.0		
Glycoletherdiaminetetraacetic acid	33.1		
Diethylenetriaminepentaacetic acid	91.2		
Cyclohexanediaminetetraacetic acid	100.0		
Sodium anthranilate	0.6		

<sup>a</sup>K<sub>2</sub>S<sub>2</sub>O<sub>8</sub> 1 m mol and NH<sub>2</sub>OH·HCl 1 m mol are presented.

<sup>b</sup>In 100 ml, blank value was subtracted.

**Table 2** Relation between organic compounds without carbonyl group and the amount of hydrogen cyanide formed<sup>a</sup>

Compounds	HCN ( $\mu$ mol) <sup>b</sup>
<i>Aromatic hydrocarbons</i>	
Benzene	12.2
Toluene	0.9
Xylene	1.8
<i>Alcohols</i>	
Methanol	5.7
Ethanol	1.1
2-propanol	3.7
<i>Amines</i>	
Methylamine <sup>c</sup>	2.9
<i>n</i> -butylamine	0.4
Ethylenediamine	3.1
1,6-hexanediamine	1.5
Triethanolamine	9.7
<i>Pyridines</i>	
Pyridine	7.8
2,2'-bipyridyl	13.2
1,10-phenanthroline	0.0

<sup>a</sup>K<sub>2</sub>S<sub>2</sub>O<sub>8</sub> 1 m mol and NH<sub>2</sub>OH·HCl 1 m mol are presented.

<sup>b</sup>In 100 ml, Blank value was subtracted.

<sup>c</sup>40% solution, 0.1 ml.

EDTA, which has two amino groups and four carboxylic groups, produced the largest amount of hydrogen cyanide of all the organic compounds tested.

Larger amounts of hydrogen cyanide are formed by the reaction of EDTA, potassium peroxodisulfate and hydroxylammonium hydrochloride when compared to the EDTA and sodium nitrite reaction.<sup>6</sup>

- 5) The amount of hydrogen cyanide from compounds without a carbonyl group is less than that from carbonyl containing compounds.

- 6) Aromatic compounds and pyridines also produced hydrogen cyanide. It was thought that the benzene ring or pyridine ring was cleaved by the reaction with potassium peroxodisulfate and hydroxylammonium hydrochloride in orthophosphoric acid solution. Almost no hydrogen cyanide is formed from 1,10-phenanthroline.

**Effects of nitrogen compounds on the formation of HCN**

The formation of hydrogen cyanide was studied using nitrogen compounds (1 m mol) in the presence of potassium peroxodisulfate (1 m mol) and EDTA (1 m mol). Some results are shown in Table 3.

The tendency of the results are as follows:

- 1) A large amount of hydrogen cyanide was formed from inorganic nitrogen compounds such as hydroxylammonium hydrochloride, hydroxylammonium sulfate, sodium nitrite and hydrazonium dihydrochloride.

**Table 3** Relation between inorganic nitrogen compounds and the amount of hydrogen cyanide formed<sup>a</sup>

Compounds	HCN ( $\mu$ mol) <sup>b</sup>
<i>Inorganic</i>	
Hydroxylammonium hydrochloride	141.0
Hydroxylammonium sulfate	130.0
Sodium nitrite	10.3
Hydrazonium dihydrochloride	1.8
Ammonium chloride	0.0
Potassium nitrate	0.0
Amidosulfuric acid	0.0
Ammonium amidosulfuric acid	0.0
Sodium azide	0.0
<i>Organic</i>	
Urea	0.0
Aminoacetic acid	0.0
Sulfanilamide	0.0

<sup>a</sup>K<sub>2</sub>S<sub>2</sub>O<sub>8</sub> 1 m mol and EDTA 1 m mol are presented.  
<sup>b</sup>In 100 ml.

- 2) Almost no hydrogen cyanide formed from ammonium chloride, potassium nitrate, amidosulfuric acid, ammonium amidosulfuric acid and sodium azide.
- 3) Almost no hydrogen cyanide formed from organic compounds such as urea, aminoacetic acid, sulfanylamide and so on.
- 4) Almost no hydrogen cyanide formed from aliphatic and aromatic amines such as methylamine, *n*-butylamine, ethylenediamine, aniline, cyclohexylamine and so on.
- 5) Hydrogen cyanide is formed by the reaction of amines and nitrous acid.<sup>6,8</sup> Therefore, it is thought that amino group is not the nitrogen source, but carbon source for cyanide formation.

### Identification of cyanide by X-ray diffraction

In order to confirm the formation of hydrogen cyanide, X-ray diffraction analysis was carried out on the precipitate obtained by the reaction of the distillate and silver nitrate solution. Results on sodium acetate, aminoacetic acid, hydroxylacetic acid, acetaldehyde, acetone, benzene and pyridine are shown in Figure 1. One to 5 mmol of each sample was used.

The X-ray diffraction peaks of cyanide appear at approximately  $2\theta = 23.9^\circ, 29.0^\circ$  (mean peak),  $38.3^\circ, 49.3^\circ$  and  $52.7^\circ$ .

Peaks, almost coincident with the standard silver cyanide, have been obtained from the precipitates. Thus, formation of hydrogen cyanide from the organic compounds is confirmed.

### Formation scheme of hydrogen cyanide

Kanno *et al.* reported the formation mechanism of cyanide ion from aniline or naphthylamine with nitrous acid.<sup>8,9</sup> They proposed the following reaction scheme. Aniline was at first converted to phenol by diazotization and then followed by nitrosation to yield *p*-nitrophenol. This product was successively decomposed by excess nitrous acid to form cyanide ion.

In the experiments previously described, it was also shown that hydrogen cyanide is formed from various kinds of organic compounds by the reaction of potassium peroxodisulfate and hydroxylammonium hydrochloride. Therefore, the ions in the reaction



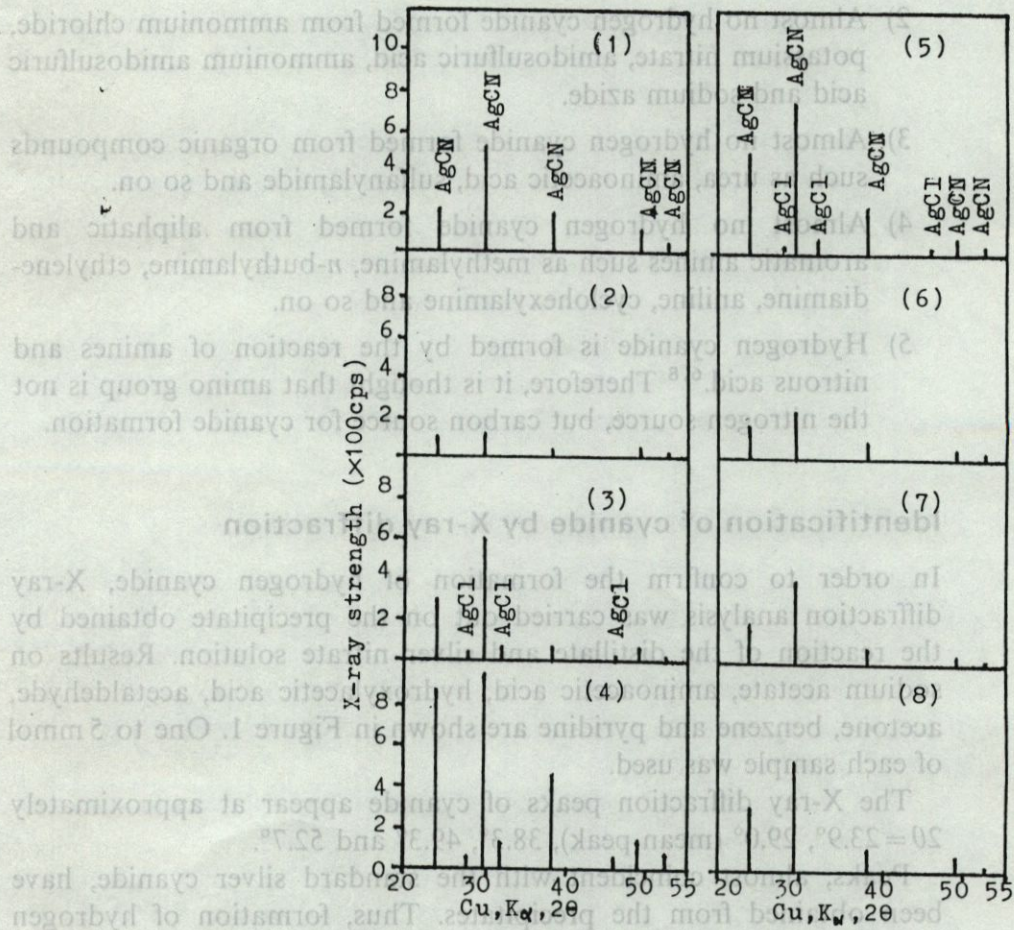


Figure 1 Identification of cyanide compounds with X-ray diffraction method.

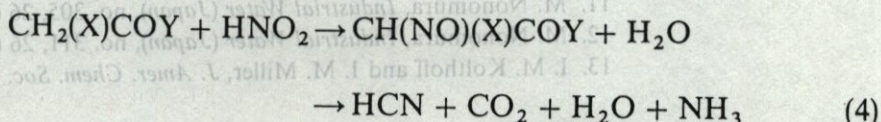
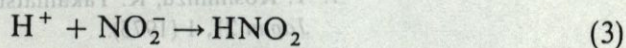
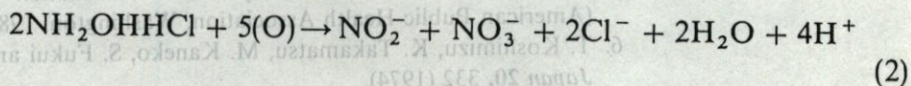
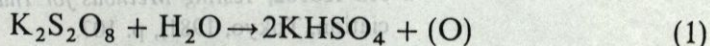
- |                               |                  |                              |
|-------------------------------|------------------|------------------------------|
| (1) Silver cyanide (standard) | (5) Acetaldehyde | Organic compounds: 1-5 m mol |
| (2) Sodium acetate            | (6) Acetone      | $K_2S_2O_8$ : 1 m mol        |
| (3) Aminoacetic acid          | (7) Benzene      | $NH_2OH \cdot HCl$ : 1 m mol |
| (4) Hydroxylacetic acid       | (8) Pyridine     | Orthophosphoric acid: 10 ml  |

medium were investigated in order to elucidate the reaction mechanism.

A solution containing sodium acetate, potassium peroxodisulfate, hydroxylammonium hydrochloride and orthophosphoric acid was distilled. The solution in the flask was removed at 10-minute intervals and analyzed by ion chromatography using a HPICE-AS1 separator column. The results showed that strong acids and acetate

ion were presented in the flask during distillation. The large peaks represent the strong acid ions such as orthophosphate, chloride and sulfate ions. Therefore, it is estimated that most of the acetate ion remained in the flask while some part of it reacted to give hydrogen cyanide. From the other ion chromatographic analysis, nitrite and nitrate ions were also detected.

Considering these results and the reaction scheme proposed by others,<sup>8,9</sup> the following scheme for hydrogen cyanide formation was proposed:



where,

X: H, NH<sub>2</sub>, OH

Y: OH, H, CH<sub>3</sub>, NH<sub>2</sub>

The carbonyl compounds represented by CH<sub>2</sub>(X)COY are acetic acid, aminoacetic acid, hydroxylacetic acid, acetaldehyde, acetone and acetamide. Potassium peroxodisulfate decomposes to give potassium hydrogen sulfate and nascent oxygen (reaction 1).<sup>13</sup> The nitrite and nitrate ions have been produced by the reaction of nascent oxygen with hydroxylammonium hydrochloride (reaction 2). The nitrite ion produced in the orthophosphoric acid solution yields nitrous acid (reaction 3). Then, during the distillation process, nitrous acid reacts with the carbonyl compounds to produce hydrogen cyanide (reaction 4).

### Acknowledgements

The author wishes to thank Dr. T. Hobo of the Tokyo Metropolitan University for help in preparing this manuscript and to Dr. H. Murata of the Tokyo Metropolitan Industrial Technology Center for the X-ray diffraction measurements.

### References

1. J. M. Kruse and M. G. Mellon, *Sewage and Ind. Waste* **23**, 1402 (1951).
2. J. M. Kruse and M. G. Mellon, *Anal. Chem.* **25**, 446 (1953).
3. F. J. Ludzack, W. A. Moore and C. C. Ruchhoft, *Anal. Chem.* **26**, 1784 (1954).
4. JIS K0102, *Testing Methods for Industrial Wastewater*, (Japanese Standards Association, Tokyo, 1981), p. 107.
5. A.P.H.A., *Standard Methods for the Examination of Water and Wastewater* (American Public Health Association, Washington, 1985), 16th ed., p. 327.
6. T. Koshimizu, K. Takamatsu, M. Kaneko, S. Fukui and S. Kanno, *J. Hyg. Chem. Japan* **20**, 332 (1974).
7. T. Koshimizu, K. Takamatsu, M. Kaneko, S. Fukui and S. Kanno, *J. Hyg. Chem. Japan* **21**, 1 (1975).
8. S. Kanno, K. Nojima and T. Ohya, *Chemosphere* **7**, 657 (1978).
9. S. Kanno, K. Nojima and T. Ohya, *Chemosphere* **9**, 415 (1980).
10. D. Owerbach, *J. Water Pollut. Control Fed.* **52**, 2647 (1980).
11. M. Nonomura, *Industrial Water (Japan)*, no. 305, 26 (1984).
12. M. Nonomura, *Industrial Water (Japan)*, no. 311, 26 (1984).
13. I. M. Kolthoff and I. M. Miller, *J. Amer. Chem. Soc.* **73**, 3055 (1951).