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FALSE DETECTION OF CYANIDE ION IN PHOTOGRAPHIC PROCESSING WASTE SOLUTIONS USING STANDARDIZED REFERENCE METHODS

MAKOTO NONOMURA

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

FUMIO NAKAGAWA

Department of Environmental Control, Fuji Photo Film Co., Ltd., 26-30, Nishiazabu 2-Chome, Minato-ku, Tokyo, 106, Japan

SHINYA MIZUSAWA, TAKASHI OHNO and HIROYUKI KOBAYASHI

Department of Image Science and Engineering, Faculty of Engineering, Chiba University, 1-33 Yayoicho, Chiba, 260, Japan

TOSHIYUKI HOBO

Department of Industrial Chemistry, Faculty of Technology, Tokyo Metropolitan University, 1-1, Fukasawa 2-Chrome, Setagaya-ku, Tokyo, 158, Japan

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Although cyanide compounds are not incorporated in photographic processing solutions, false detection of cyanide ion is often encountered during the determination of total cyanide by various standardized methods such as ISO, ANSI and JIS. Various organic compounds and nitrogen compounds in the processing solutions were examined because of this false detection. The results suggest that hydrogen cyanide is formed by a reaction between these compounds during the distillation process for the separation of total cyanide, even though ISO, ANSI and JIS were used. The results support the following three mechanisms of cyanide formation involved in the process: (1) Hydroxylammonium salts reacts with another ingredient, formaldehyde, to form formaldoxime, which then decomposes to HCN. (2) Hydroxylammonium is oxidized by air to form nitrite ion, which subsequently reacts with organic compounds such as aminocarboxylic acids and aromatic amines (the colour-developing agent) to form HCN. (3) Potassium permanganate oxidizes aromatic amines to form HCN.

KEY WORDS: Cyanide formation, photographic waste solution, ISO, ANSI, JIS.

INTRODUCTION

The testing method for cyanide compounds in photographic effluent was issued by the American National Standard Institute (ANSI).[1] Several standard methods such as the International Standard Organization (ISO) methods,[2] the Standard

Methods,[3] the Japanese Industrial Standard (JIS),[4] etc. are used for the determination of total cyanide in waste solutions after photographic processing.

Although cyanide compounds are not incorporated in photographic processing solutions, false detection of cyanide ion is often encountered during the determination of total cyanide. Since various kinds of organic compounds and nitrogen compounds are incorporated in photographic processing solutions, hydrogen cyanide (HCN) is apparently being formed by the reaction of these compounds during the distillation process.

Previously, one of the authors reported that cyonide ions have been detected in wastewater discharged from various factories that do not handle any cyanide compounds.[5] Furthermore, the effects of various organic compounds and nitrogen compounds on the formation of HCN and the pertinent mechanism were reported.[6] A pretreatment method for the determination of total cyanide has also been published.[7]

This paper describes the effects of organic compounds and nitrogen compounds on the formation of cyanide ion within a photographic processing waste solution during analytical processing and a discussion of the probable mechanism.

EXPERIMENTAL METHODS

Apparatus and Reagents

Apparatus and reagents have been previously reported except for the following:[7] The distillation apparatus indicated in the ISO.[2] ANSI[1] and JIS[4] method, as used for the separation of total cyanide. All chemicals used were of the highest grade commercially available.

Procedure

The total cyanide determination procedure is based on the ISO,[2] ANSI[1] and JIS[4] methods. In order to investigate the effects of organic compounds and nitrogen compounds (i.e., included in the photographic processing solutions) on cyanide formation, 1 mmol of the test compound was added to the solution (ca. 250 ml) to be distilled together with 1 mmol hydroxylammonium sulfate or sodium nitrite. The compounds tested were EDTA, formaldehyde and aromatic amines. Likewise, the formation of HCN from 1 mmol organic compounds and 0.2 mmol potassium permanganate was examined.

The distillation procedure for total cyanide was basically the same as that described in standard methods. The cyanide ion in the distillate was determined by the pyridine-pyrazolone method.[4] In addition, the presence of cyanide ion was confirmed by ion chromatography.[8]

RESULTS AND DISCUSSION

Reaction Between Hydroxylammonium Sulfate and Organic Compounds

The list of ingredients and the range of concentrations in typical colour negative and paper processing solutions are presented in Table 1.

Table 1 Typical components in photographic processing solution

Component	*Concentration (g/l)*
Colour developing agent A	0.5–1.3
Colour developing agent B	0.2–0.6
Water softener	0.1–3.5
EDTA · Fe(III) · NH_4 complex	15–25
Formaldehyde (37%)	0–0.25
Diethylene glycol	0–3.5
Benzyl alcohol	0–3.5
Sodium hydroquinone monosulfonic acid	0–0.5
Potassium carbonate	10–14
Potassium phosphate	0–0.6
Fluorescence bleaching agent	0.1–0.4
Ammonium thiosulfate	15–28
Sodium sulfite	2.5–5.5
Tin(II) chloride	trace
Ammonium bromide	13–19
Ammonium nitrate	0.5–1.5
Aqueous ammonia (28%)	0–1.4
Hydroxylammonium sulfate	0–0.9

Table 2 Formation of hydrogen cyanide by the reaction of various organic compounds and hydroxylammonium sulfate

Organic compound[a]	*HCN formed (μg)*		
	JIS	*ISO*	*ANSI*
EDTA	1.0	3.2	23.3
EDTA · Fe(III) · NH_4	22.2	12.2	41.1
NTA	2.2	7.1	10.8
Diethylene glycol	<0.5	<0.5	<0.5
Benzyl alcohol	<0.5	<0.5	<0.5
Acetic acid	<0.5	<0.5	<0.5
Formaldehyde	25.3	463	673
p-Phenylenediamine · 2HCl	<0.5	<0.5	<0.5
N, N-Diethyl-p-phenylenediamine · 2HCl	<0.5	<0.5	1.6
CD-2	<0.5	<0.5	<0.5
CD-3	<0.5	0.7	<0.5

[a]Organic compound, 1 mmol; $(NH_3OH)_2SO_4$, 1 mmol; detection limit; 0.5 μg as HCN.

Nitrogen compounds such as hydroxylammonium sulfate and ammonium nitrate, and organic compounds such as EDTA, diethylene glycol, benzyl alcohol, formaldehyde, and aromatic amines (the colour developing agent) are present in photographic processing solutions. The effects of these reagents on cyanide formation were examined using the three standard methods. The results are presented in Table 2.

A small amount of HCN was formed from aminocarboxylic acids such as EDTA and NTA in the three standard methods. Increased formation of HCN

Table 3 Formation of hydrogen cyanide by the reaction of various organic compounds and sodium nitrite

Organic compound[a]	*HCN formed* (μg)[b]		
	JIS	*ISO*	*ANSI*
EDTA	121	0.7	15.1
EDTA · Fe(III) · NH_4	15.4	1.2	2.6
NTA	50.1	0.5	3.0
Diethylene glycol	<0.5	<0.5	<0.5
Benzyl alcohol	<0.5	<0.5	<0.5
Acetic acid	<0.5	<0.5	<0.5
Formaldehyde	<0.5b	15.2	<0.5
p-Phenylenediamine · 2HCl	11.7c	0.9	1.9
N, N-Diethyl-p-phenylenediamine · 2HCl	22.8c	1.1	136
CD-2	6.0c	<0.5	16.6
CD-3	3.2c	<0.5	27.0

[a]Organic compound, 1 mmol; $NaNO_2$, 1 mmol; detection limit; 0.5 μg as HCN.
[b]b, turbid; c, light brown.

from EDTA · Fe(III) · NH_4 was observed. This result suggested that hydroxylammonium sulfate is oxidized by Fe(III).

Hydrogen cyanide was not formed from diethylene glycol, benzyl alcohol, acetic acid, aromatic amines or the colour developing agents (CD-2, CD-3). On the other hand, sizable levels of HCN were formed from formaldehyde. Owerbach[9] reported that formaldoxime salt, which is formed from formaldehyde and hydroxylammonium salt, is decomposed to yield HCN during distillation.

Reaction Between Sodium Nitrite and Organic Compounds

It is known that cyanide ion is formed by a reaction between sodium nitrite and organic compounds.[10,11] Our concern is whether cyanide ion is formed in the presence of sodium nitrite and photographic processing solutions. The results obtained by the three standard methods are presented in Table 3.

Hydrogen cyanide was not formed from diethylene glycol, benzyl alcohol or acetic acid. On the other hand, HCN was formed from EDTA, EDTA · Fe(III) · NH_4, NTA, aromatic amines and the colour developing agents by the reaction with sodium nitrite, even though the three standard methods were used. When the ISO method was used, decreased formation of HCN was observed as compared with the other two standard methods. However, increased formation of HCN from formaldehyde was observed. This was due to the fact that nitrite ion was reduced to hydroxylammonium by tin(II) chloride.

When the JIS method was used, the distillate had a light brown colour. This coloration may induce a positive error in the absorbance measurement.[12]

Air Oxidation of Hydroxylammonium

Hydroxylammonium sulfate is also one of the ingredients of the colour developing

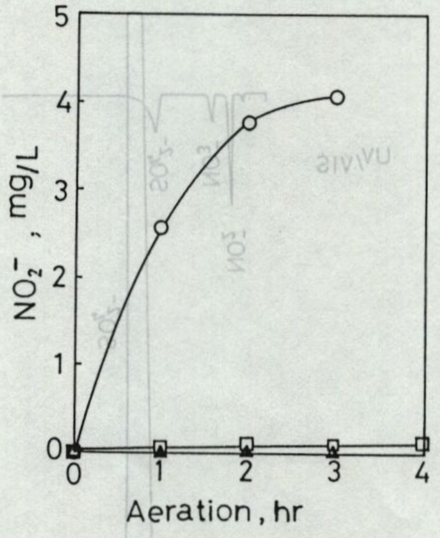

Figure 1 Formation of nitrite ion by air oxidation; ○: hydroxylammonium sulfate (2 g/l, pH 11.0); △: hydroxylammonium sulfate (2 g/l, pH 3.9); □: ammonium nitrate (10 g/l, pH 8.3).

solutions.[13] Haist[13] reported that it is unstable in alkaline solution and decomposes as follows:

$$3NH_2OH \rightarrow N_2 + NH_3 + 3H_2O. \tag{1}$$

Nichols[14] and James,[15,16] however, reported that nitrogen or nitrous oxides are formed by the reaction between hydroxylammonium and silver halides:

$$2NH_2OH + 2AgBr \rightarrow 2Ag + N_2 + 2HBr + 2H_2O \tag{2}$$

$$2NH_2OH + 4AgBr \rightarrow 4Ag + N_2O + 4HBr + H_2O. \tag{3}$$

Hughes[17] and Moews[18] also reported that nitrous acid and nitrous oxide were formed by air oxidation of hydroxylammonium.

In order to clarify the formation of nitrite ion from nitrogen compounds, hydroxylammonium and ammonium nitrate were oxidized by air. The air flow rate was 1 l/min and nitrite ion was determined by the l-naphthylamine colorimetric method.[19] The results are shown in Figure 1. In alkaline solution, hydroxylammonium is oxidized by air to give nitrite ion. On the other hand, the amount was small in the acidic solution. Nitrogen oxide disappeared because of aeration in the acidic solution. Furthermore, nitrite ion was not detected in the case of ammonium nitrate.

Ion chromatographic analyses using an anion separator column (HPIC-AS4A), and UV/VIS and conductivity detectors, were performed after hydroxylammonium sulfate had been oxidized with air for 3 hours. The results are shown in Figure 2. They indicate that nitrite ion is formed by the following air oxidation of hydroxylammonium sulfate:

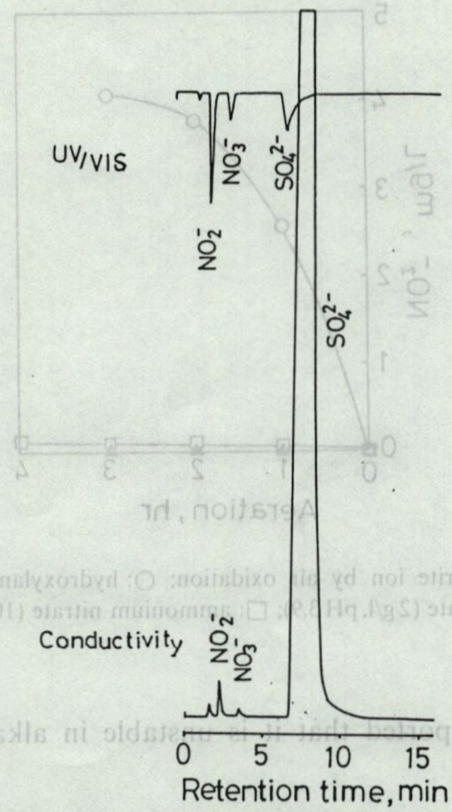

Figure 2 Ion chromatographic analyses after air oxidation of hydroxylammonium. Apparatus: Dionex 2010i. Column: HPIC-AS4A. Eluent: 1.0 mM $NaHCO_3$ + 1 mM Na_2CO_3. Detector: Conductivity (fs; 30 mS), UV/VIS (0.16 aufs). Hydroxylammonium sulfate (2 g/l, pH 11.0). Five-fold dilution after aeration for 3 hours.

$$2NH_2OH + O_2 \rightarrow N_2O + 3H_2O \tag{4}$$

$$N_2O + H_2O + O_2 \rightarrow 2HNO_2 \tag{5}$$

Reaction Between Potassium Permanganate and Organic Compounds

Sulfur dioxide is formed during the distillation of total cyanide and it interferes with the determination of cyanide ion, because reducing agents such as sodium sulfite and ammonium thiosulfate are incorporated in the photographic processing waste solution. It is therefore necessary that the distillation process is repeated after the first distillate has been treated with potassium permanganate.[4]

In order to clarify the possibility of HCN formation through the reaction of potassium permanganate with the organic ingredients, the reaction between potassium permanganate and organic compounds in a photographic processing solution was examined. The results obtained by the standard methods are presented in Table 4.

The aromatic amines react with potassium permanganate to form HCN.

Table 4 Formation of hydrogen cyanide by the reaction of various organic compounds and potassium permanganate

Organic compound[a]	*HCN formed* (μg)		
	JIS	*ISO*	*ANSI*
EDTA	<0.5	6.3	7.5
EDTA · Fe(III) · NH_4	2.3	6.7	2.4
NTA	<0.5	1.4	5.6
Diethylene glycol	<0.5	<0.5	<0.5
Benzyl alcohol	<0.5	<0.5	<0.5
Acetic acid	<0.5	<0.5	<0.5
Formaldehyde	<0.5	<0.5[b]	<0.5[b]
p-Phenylenediamine · 2HCl	46.8	29.3	33.4
N, N-Diethyl-p-phenylenediamine · 2HCl	32.0	6.6	27.8
CD-2	74.4	82.9	55.0
CD-3	17.4	23.9	26.5

[a]Organic compound, 1 mmol; $KMnO_4$, 0.2 mmol; detection limit; 0.5 μg as HCN.
[b]turbid.

Therefore, it is expected that HCN will be formed from the distilled aromatic amines during redistillation in the presence of an excess of potassium permanganate.

Small amounts of HCN were formed from organic compounds such as aminocarboxylic acids. However, almost no HCN was formed from formaldehyde, diethylene glycol and other such compounds.

Formation Mechanism of Hydrogen Cyanide

The formation mechanism of HCN from photographic processing waste solutions during analytical processing can be summarized as follows.

1) Reaction between Hydroxylammonium and Formaldehyde

As Owerbach[9] has already reported, hydroxylammonium salt reacts with formaldehyde to form formaldoxime, which then decomposes to give HCN during distillation:

$$NH_2OH + HCHO \rightarrow HCH{=}NOH + H_2O \rightarrow HCN + 2H_2O \qquad (6)$$

2) Reaction between Nitrous acid and organic compounds

Hydroxylammonium in the photographic processing solution is oxidized by air to form nitrous acid:

$$4NH_2OH + 5O_2 \rightarrow 2NO_2^- + 2NO_3^- + 4H_2O + 4H^+ \qquad (7)$$

$$H^+ + NO_2^- \rightarrow HNO_2. \qquad (8)$$

Nitrous acid reacts with aminocarboxylic acids and aromatic amines to give HCN:

$$R(NH_2)COOH + HNO_2 \rightarrow R(NO)(NH_2)COOH \rightarrow HCN \quad (9)$$

$$Ar{-}NH_2 + HNO_2 \rightarrow Ar{-}N{=}N{-}OH + H_2O \rightarrow HCN. \quad (10)$$

3) Reaction between Potassium Permanganate and aromatic amines

Aromatic amines also react with potassium permanganate to form HCN during distillation. In addition, the diazonium salt formed by the reaction of the aromatic amine and nitrous acid is oxidized by potassium permanganate to give HCN:

$$Ar{-}NH_2 + KMnO_4 \rightarrow HCN \quad (11)$$

or

$$Ar{-}NH_2 + HNO_2 \rightarrow Ar{-}N{=}N{-}OH + H_2O \quad (12)$$

$$Ar{-}N{=}N{-}OH + KMnO_4 \rightarrow HCN. \quad (13)$$

Therefore, HCN formation during the distillation of the processing waste solution is induced by any of the reactions already mentioned.

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