FACTORS AFFECTING CYANIDE GENERATION IN CHLORINATED WASTEWATER EFFLUENT MATRIX

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ABSTRACT: False positives for cyanide analysis in wastewaters have been reported. We examined the effects of storage time at high pH and of pH adjustments on the cyanide levels. Cyanide levels changed within the holding time allowed by *Standard Methods*. We also studied the difference in cyanide levels using two disinfection conditions -- breakpoint chlorination and chloramination. Glycine was used as the precursor to study the cyanide formation pathways. Under breakpoint chlorination conditions, cyanide formation is complete relatively quickly and detectable cyanogen chloride is produced. On the other hand, chloramination yields cyanide through a relatively slow, base-catalyzed reaction. Chloramination followed by dechlorination with sodium arsenite and addition of NaOH results in cyanide levels that increase significantly upon reanalysis in the first 24 hours and then remain relatively constant after that time. Cyanogen chloride (CNCl) was <5 ppb in samples disinfected with chloramination. Mechanisms are proposed that explain the very different cyanide results that are obtained when disinfection is carried out under breakpoint chlorination conditions versus chloramination conditions.

KEYWORDS
cyanide generation, wastewater treatment, holding time, precursors, interferences, analytical methods

INTRODUCTION AND BACKGROUND

Recent studies in wastewater matrices have suggested the presence of uncharacterized positive interferences affecting the analysis of total cyanide using colorimetric procedures such as EPA 335.4 (U.S. EPA, 1993) and *Standard Methods* 4500-CN (APHA/AWWA/WEF, 1998). As a result of these studies, attention has begun to focus on the reliability of currently accepted cyanide analytical methods. False positives resulting from cyanide formation during sample storage at high pH have recently been reported by Weinberg, et al. (Weinberg et al., 2005). The city of San Jose concluded that cyanide was being generated after collection, during the preservation of wastewater effluent samples to which NaOH was added to adjust the pH to 12 (City of San Jose, 2004). Studies conducted in the Los Angeles County Sanitation Districts' laboratories indicated that some of the approved preservation protocols could give rise to cyanide formation in chlorinated wastewater effluent matrices (Khoury et al., 2005).

The Sanitation Districts' laboratories have carried out extensive studies on cyanide formation by testing samples from several wastewater treatment plants. The results have indicated that cyanide levels are generally below reporting limits when samples are analyzed immediately without pH adjustment, irrespective of the dechlorinating agent used. However, a significant increase (>10 μg/L) of cyanide was found in samples taken after chlorination of the secondary effluent, when dechlorinated with sodium arsenite and then preserved to pH >12 (Khoury et al., 2005).

Standard Methods suggests a holding time of 14 days for samples preserved to pH ≥ 12, using sodium hydroxide to retard the loss of volatile hydrogen cyanide by converting it to its non-volatile ionic form. The study presented in this paper is focused on the effects of the storage time between sampling and analysis for cyanide within the holding time of 14 days. When samples preserved to pH 12 were analyzed over a period of 48 hours within a *Standard Methods*-recommended holding time, it was observed that the cyanide levels increased with time. This indicates a possibility that an *in-situ* cyanide generation reaction is in progress at pH12.

Chlorination is a well-developed and widely used process for disinfection. There are numerous pros and cons related to using either chloramination or breakpoint chlorination in disinfecting wastewater streams. Chloramination would decrease several regulated disinfection by-products (DBPs), i.e., total trihalomethanes (THMs), however it would increase the production of the potent carcinogen N-nitrosamines (Mitch and Sedlak, 2002). Breakpoint chlorination, on the other hand, would decrease the production of N-nitrosamines (Mitch and Sedlak, 2002), but may introduce other by-products, i.e., cyanogen chloride (CNCl) (Shang et al., 2000) and THMs. In this study, cyanide generation is examined under two disinfection conditions -- breakpoint chlorination and chloramination.

Possible mechanisms for cyanide formation in water and wastewater treatment processes have been identified in laboratory scale experiments. The mechanism of cyanide and CNCl formation from glycine in water under free chlorine conditions has been reported by Na and Olson (2006). Monochloramine has been shown to react with formaldehyde and eventually yield HCN (Pedersen et al., 1999); organocyanide compounds (cyanocobalamin and coenzyme vitamin B12) release free or metal-complexed cyanide upon chlorination (Yi et al., 2002); solutions of L-serine that were chlorinated and subsequently dechlorinated were shown to produce cyanide (Zheng et al., 2004a); reaction of nitrite with aromatic compounds can produce cyanide (Zheng et al., 2004b); microorganisms have been shown to be capable of producing cyanide (Brandl, 2005); less than stoichiometric chlorination of thiocyanate can liberate free cyanide (Zheng et al., 2004c); and, it was found that phenol reacts with nitrous acid to produce cyanide ions (Adachi et al., 2003). The potential for chloramination to yield cyanide from organic compounds was demonstrated in earlier experiments using synthetic solutions spiked with select precursor organics such as ascorbic acid, humic acid, D-ribose, and 2-furaldehyde (Carr et al., 1997).

Amino acids have been reported as potential precursors of the disinfection byproduct CNCl in chlorinated drinking water (Sawamura Et al., 1982; Hirose et al., 1989). Glycine, among 17 amino acids, has been proved to yield the most CNCl after chlorination (Lee et al., 2006). In this study, glycine was spiked in water samples collected from secondary effluents, before ammonia addition, to study the mechanisms of the production of cyanide and CNCl. Under laboratory controlled conditions, chlorine and chloramines were dosed according to the wastewater

treatment conditions. The major objectives of this study were to confirm the cyanide formation mechanisms and to provide feasible suggestions for wastewater disinfection operations.

METHODS

Cyanide Analysis. Total cyanide measurements were conducted using the Midi Distillation System followed by manual colorimetric analysis [EPA 335.4, Method 4500-CN-C (APHA/AWWA/WEF, 1998)]. The sample volume used for this study was 50mL and all samples were distilled into 50 mL NaOH absorbing solution, resulting in a dilution factor of 1. The method detection limit (MDL) is 1 µg/L. The lowest point on the calibration curve (the minimum level or ML) is 5 µg/L; the reporting limit is 5 µg/L. An estimated value was reported for data that was between 1 and 5 µg/L.

Cyanogen Chloride Analysis. CNCl measurements were made colorimetrically, following *Standard Methods* 4500-CN-J (APHA/AWWA/WEF, 1998). The lowest point on the calibration curve (the minimum level or ML) is 5 µg/L; the reporting limit is 5 µg/L. An estimated value was reported for data that was between 1 and 5 µg/L.

Cyanate and Thiocyanate Analysis. Cyanate (CNO^-) and thiocyanate (SCN^-) were determined by gradient elution ion chromatography using the DX-500 Dionex Ion Chromatograph (CSDLAC Method 262A CNO, and Method 256C SCN, 2006). The method detection limit (MDL) for both CNO and SCN is 1 µg/L. The lowest point on the calibration curve (the minimum level or ML) is 5 µg/L; the reporting limit is 5 µg/L. An estimated value was reported for data that was between 1 and 5 µg/L.

Sample Matrices. Wastewater used in this study was collected from the final effluents of tertiary water reclamation plants (WRPs) operated by the Sanitation Districts. These plants are the San Jose Creek East Water Reclamation Plant (SJC East WRP), the San Jose Creek West Water Reclamation Plant (SJC West WRP) and the Long Beach Water Reclamation Plant (LB WRP). Average flow rates treated at these plants are 55, 29, and 5 million gallons per day (MGD), respectively. All the plants are equipped with primary clarifiers, activated sludge processes with biological nitrogen removal, final clarifiers, media filters, and chlorine contact tanks. Chloramination is used for disinfection at these plants; ammonia and chlorine are introduced to the secondary effluent. Effluent from the chlorine contact tank is typically dechlorinated using sulfur dioxide or sodium bisulfite before discharge to receiving water bodies.

Dechlorination and pH Adjustment. *Sodium Arsenite*. 0.1N sodium arsenite was added at a rate of 3.0 mL per 500 mL of sample. Before the cyanide analysis, all samples were retested to ensure complete removal of chlorine and other oxidizing agents. *Sodium Thiosulfate*. The required amount of 1.0% $Na_2S_2O_3$ solution for complete dechlorination was determined by the iodometric method (Method 4500-Cl-B).

pH Adjustment. When pH adjustment was required, the pH was measured using a calibrated meter. The ambient pH of the final effluents from treatment plants was usually around 7.4.

Precursor study. Glycine was obtained from Sigma-Aldrich. The stock solution was prepared with distilled, deionized (DI) water and stored in a refrigerator for no more than two weeks. The molar ratio of chlorine (or chloramine) to glycine was 2.

RESULTS AND DISCUSSION

Effect of sample storage at high pH

Section 4500-CN-B of *Standard Methods* 20th Ed. indicates that cyanide samples should be analyzed immediately, but if immediate analysis is not possible, then the samples should be preserved by adding NaOH pellets or strong NaOH solution to raise the sample pH to 12 or 12.5. The method allows a 14-day holding time for preserved samples. Both of the approved protocols were studied under chloramination conditions, and it was observed that immediate analysis gave cyanide levels below the laboratory's reporting limit of 5 µg/L, whereas high pH preservation of the same sample gave higher cyanide levels. Reanalysis of the preserved sample, upon storage for 1 day, showed an additional increase in the cyanide level on the second day. Figure 1a clearly shows that three approved protocols (i.e. immediate analysis at ambient pH, pH12 on the first day, and pH12 on the second day) for cyanide analysis are giving inconsistent results. Each different experiment number indicates a different day. Another set of experiments was performed under chloramination conditions to further study the effect of storage time on the preserved samples at shorter time intervals. The chlorinated final effluent sample was dechlorinated using sodium arsenite and preserved to pH12 and was reanalyzed at time intervals of 15min, 1hr, 2hrs, 3hrs, 4hrs, 5hrs, and 6hrs, 24hrs, and 48hrs (Figure 1b). The results indicate that there is a significant increase within the first hour and that the cyanide level continues to increase for up to 4 hrs and stays relatively constant for up to 48 hrs. The preservation to pH12 is supposed to protect the sample integrity and should not cause an increase or decrease in the cyanide level. Our results indicate that the cyanide level fluctuates and also shows a significant increase upon reanalysis. The same experiment in deionized water showed no increase in the cyanide level upon storage at high pH. This indicates the presence of precursors, which generate cyanide in wastewater samples under strongly basic preservation conditions.

Figure 1a. Effects of storage time on cyanide levels under chloramination conditions.

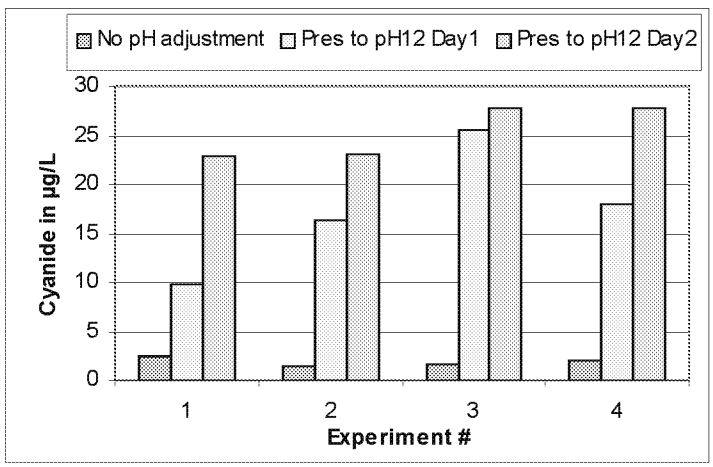
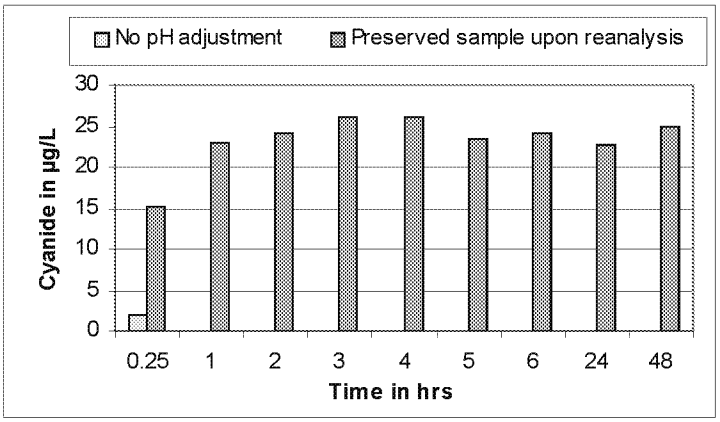


Figure 1b. Effects of storage time on cyanide levels under chloramination conditions.



Effect of pH adjustment

Grab samples of plant-chlorinated final effluent were dechlorinated with sodium arsenite and analyzed under three conditions: without pH adjustment, preservation to high pH, and adjusting the preserved sample back to its initial pH. All analyses were performed immediately within 15 minutes. The cyanide level found was below the reporting limit of 5 µg/L for the sample that was not pH adjusted. The same sample, when preserved to pH12, showed an increase in the cyanide level. Under breakpoint conditions, upon immediately changing the preserved sample back to its initial pH the cyanide level remained relatively constant (Table 1); however under chloramination, the level dropped significantly (Table 2). Each different experiment number indicates a different day.

Table 1. Effects of pH adjustments on cyanide level under breakpoint chlorination.

	Cyanide level (analyzed immediately) in µg/L		
Experiment #	No pH adjustment	Preservation to pH12	pH12 sample to initial pH
1	E3.0	16.9	15.0
2	E1.7	8.9	5.3

Note: E = Estimated value (values between 1 µg/L and 5 µg/ L)
All samples = Final effluent dechlorinated with sodium arsenite
pH12 = Dechlorinated effluent adjusted to pH12 with 50% sodium hydroxide

Table 2. Effects of pH adjustments on cyanide level under chloramination.

	Cyanide level (analyzed immediately) in µg/L		
Experiment #	No pH adjustment	Preservation to pH12	pH12 sample to initial pH
1	E1.5	16.3	6.5
2	E1.7	25.5	10.3
3	E2.1	18	6.2

Note: E = Estimated value (values between 1 µg/L and 5 µg/L)
All samples = Final effluent dechlorinated with sodium arsenite
pH12 = Dechlorinated effluent adjusted to pH12 with 50% sodium hydroxide

An additional experiment was performed to further investigate the effects of the timing between the pH adjustments on the cyanide levels. Plant chlorinated final effluent sample was collected, the initial pH was measured, and the sample was dechlorinated using sodium arsenite. The sample was then preserved to high pH and adjusted back to the initial pH at different time intervals.

Under chloramination conditions it was observed that if the pH was adjusted back to the initial pH within 4 to 5 hrs, the cyanide level dropped rapidly. However, if the sample was stored at pH12 for about 24 hrs and then adjusted back to the initial pH, the cyanide level stayed relatively the same as the pH12 sample (Table 3). These experiments indicate that under chloramination conditions cyanide generation is a slow reaction, which may take about 24 hrs under highly basic conditions to go to completion. Once this reaction is completed, if the pH is adjusted back to the initial pH, the cyanide level remains relatively constant. However, if the pH is adjusted back to the original sample pH within first 4 to 5 hrs, the cyanide level drops significantly.

Table 3. Effect of time between re-adjustment of dechlorinated preserved final effluent sample back to the initial pH of the sample after chloramination.

Time between adjustment of preserved sample to initial pH (Hours)	Preservation to pH12 CN (µg/L)	pH12 sample adjusted to initial pH CN (µg/L)
0.25	18.0	6.2
1	NA	12.4
2	NA	9.4
3	NA	12.1
4	NA	13.3
5	NA	17.7
24	27.8*	24.6

Note: For the above sample cyanide level for immediate analysis = E 2.1 µg/L
NA = not analyzed
* = Preserved sample, which was immediately adjusted to pH12 upon sampling, was reanalyzed 24 hr later

Free Chlorination/Breakpoint Chlorination and Chloramination

Amino acids have been cited as potential CNCl and halogenated nitrile precursors (Larson et al., 1994; Westerhoff et al., 2002). Lee and co-authors (2006) did screening experiments on 17 amino acids and concluded that glycine would yield the most CNCl after chlorination. Pedersen et al. (1999) also proposed a mechanism for CNCl formation from the reaction of monochloramine with formaldehyde. Formaldehyde, also a common DBP, is formed during ozonation or chlorination of waters containing natural organic matter (Weinberg et al., 1993; Glaze et al., 1989; Richardson 1998) and during chlorination through reaction of glycine with monochloramine (Hand et al., 1983). Therefore, a series of bench-scale studies was designed to monitor four components: cyanide, CNCl, cyanate (CNO), and thiocyanate (SCN) concurrently during breakpoint chlorination and chloramination conditions, using glycine as the precursor.

Yields of these four compounds in glycine-spiked secondary, shown in Tables 4 and 5, were a complex function of free chlorine and pre-formed chloramine dose. In Table 4 (Bench study A), high cyanide yields, 22 µg/L (immediate analysis) and 16 µg/L (after 24-hour storage), were found in preserved sample (pH>12), after chlorination with free chlorine and dechlorination with sodium arsenite. Upon chloramination, however, cyanide increases from 7 µg/L (immediate analysis) to 31 µg/L (after 24-hour storage). It indicates that the formation of cyanide is relatively rapid in the free chlorine reaction compared to chloramination reactions. The chloramination results also agree with our observations on sample storage at high pH, that is—the cyanide level shows a significant increase upon reanalysis the next day.

The CNCl concentration was high in the sample that was disinfected by free chlorine and then dechlorinated without the pH adjustment. The same sample, when preserved to pH12, showed a decrease in CNCl and an increase in cyanate, indicating the hydrolysis of CNCl to cyanate at high pH, as expected. Thiocyanate, however, was not present in any sample. The same trend is shown in Table 5 (Bench Study B) when the study was run on a different sample of secondary effluent on a different day. The data in parentheses in Tables 4 and 5 are simply the analysis of the original samples after 24 hours (marked as "2nd day").

Table 4. Bench Study A --Analysis of cyanide, CNCl, CNO, and SCN in glycine spiked secondary effluents, in µg/L

Description	Cyanide (2nd day)	CNCl (2nd day)	CNO (2nd day)	SCN (2nd day)
glycine spiked SE, free chlorine (5ppm residual), As	E3 (E 1.4)	44 (26)	23 (25)	< 5 (< 5)
glycine spiked SE, free chlorine (5ppm residual), As, pH 12	22 (16)	7 (< 5)	160 (158)	< 5 (< 5)
glycine spiked SE, chloramine (5ppm residual), As	E 1.7 (< 3)	E 2 (E 1.7)	10 (12)	< 5 (< 5)
glycine spiked SE, chloramine (5ppm residual), As, pH12	7 (31)	12 (< 5)	< 5 (< 5)	< 5 (< 5)

Note: SE = Secondary effluent before the ammonia addition
As = Sodium arsenite

Table 5. Bench Study B -- Analysis of cyanide, CNCl, CNO, and SCN in glycine spiked secondary effluents, in µg/L

Description	Cyanide (2nd day)	CNCl (2nd day)	CNO (2nd day)	SCN (2nd day)
Glycine spiked SE, free chlorine (3.2ppm residual), As	E2.8 (E3.1)	80 (30)	20 (18)	<5 (<5)
Glycine spiked SE, free chlorine (3.2ppm residual), As, pH 12	32 (30)	E1.1 (<5)	92 (73)	<5 (<5)
Glycine spiked SE, chloramine (2.5ppm residual), As	<5 (<5)	E1.7 (<5)	<5 (<5)	<5 (E1.6)
Glycine spiked SE, chloramine (2.5ppm residual), As, pH 12	18 (31)	11 (<5)	<5 (<5)	<5 (<5)

Because of the discovery that CNCl was formed in these Bench Studies, a short investigation of the levels of these four components was also carried out using disinfection conditions in our treatment plants, without glycine spiking. Samples of secondary effluent, which were disinfected with chloramination in the laboratory, and final effluent samples from the treatment plant, and outfall samples were analyzed immediately for cyanide, CNCl, CNO, and SCN. The effect of reducing agents in CNCl formation was also studied. Sodium thiosulfate, sodium arsenite, or bisulfite (for outfall sample) were used as dechlorinating agents. Table 6 shows that cyanide, CNCl, SCN, and CNO were all below their reporting limits for both the SJC East WRP and the Long Beach WRP.

Table 6. Cyanide and CNCl formation study on samples collected from secondary effluents and final effluent, in µg/L

Description	Cyanide	CNCl	Cyanate	SCN
SJC SE, chloramine (4.8ppm residual), thio	<5	<5	<5	<5
SJC SE, chloramine (4.8ppm residual), As	<5	E1.4	<5	<5
LB SE, chloramine, As (5/16/06)	E1.4	E2.5	na	na
LB SE, chloramine, As (5/19/06)	E1.7	E3.1	na	na
Outfall (bisulfite dechlorination)	E 1.4	E 2	< 5	< 5

Note: SJC SE = Secondary effluents from SJC East WRP, chloramine dosed in the lab
LB SE = Secondary effluents from LB WRP, chloramine dosed in the lab
Outfall = SJC East WRP
Thio = Samples dechlorinated with sodium thiosulfate

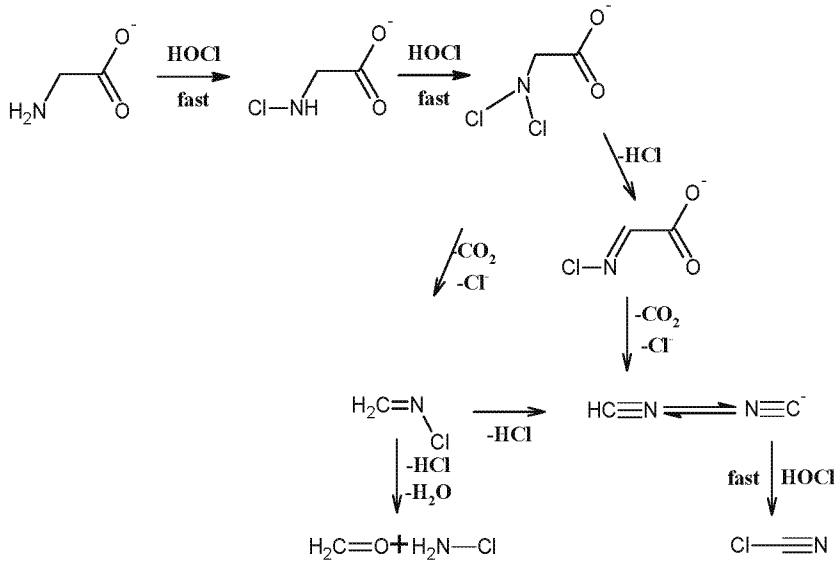
Mechanisms

Observations from cyanide formation studies are:

Disinfection with free chlorine / breakpoint chlorination:

1. When the sample was at initial pH, the cyanide level was below 5 ug/L.
2. CNCl was found in samples at initial pH.
3. When preserved to pH 12, the cyanide level increases significantly upon immediate analysis.
4. When preserved to pH 12 then adjusted back to the initial pH immediately, the cyanide level remains.

Based on the work presented here and on previous work of Na et al. (2006), the cyanide formation pathway from the reaction of glycine with chlorine is proposed here.



Pathway I. Cyanide formation from the chlorination of glycine (Na and Olson, 2006)

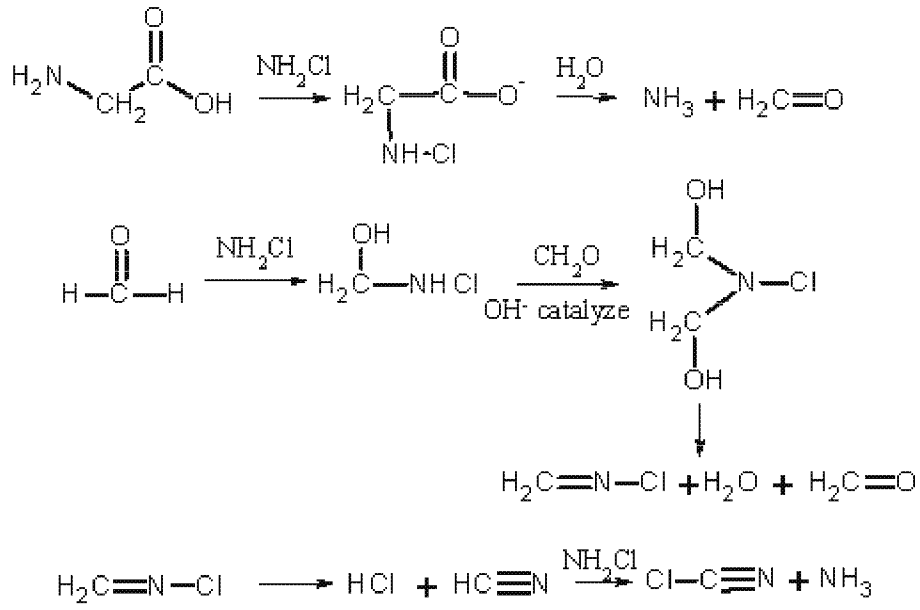
Pathway 1. N-chloroglycine and N,N-dichloroglycine are formed rapidly from the chlorination of glycine. N,N-dichloroglycine then decays to cyanide (Sawamura et al., 1982) and cyanide reacts with free chlorine to produce CNCl. At initial pH, therefore, no cyanide is found but detectable CNCl is observed (Table 4 and 5). Detectable CNCl at initial pH is due to the fast decay of N,N-dichloroglycine when an excess of chlorine is present, in spite of the use of dechlorinating agent afterwards.

In preserved samples (pH >12), arsenite is in the form of $As(OH)_2O^-$ (Dodd et al., 2006), a much stronger nucleophile of As(V) under basic conditions, which makes the cyanide formation go to completion much faster compared to the nucleophilic substitution that occurs at initial pH. Table 1 indicates that cyanide was detected at pH12 and remains relatively the same upon adjusting the pH back to initial pH. It is also true in glycine spiked secondary effluents as shown in Table 4 and 5. CNCl, however, dropped significantly due to its hydrolysis to CNO at high pH. As shown in Table 4, CNCl decreases from 44 ppb to 7 ppb and CNO increases from 23 ppb to 160 ppb when pH is adjusted from initial to pH >12.

B. Disinfection with chloramination:

1. When the sample was at initial pH, the cyanide level found was below the reporting limit of 5 ug/L.
2. No CNCl was found in samples at initial pH.
3. When preserved to pH 12, a significant increase within the first hour was observed and the cyanide level continued to increase and stayed relatively constant for up to 48 hours.
4. When preserved to pH 12 then adjusted back to the initial pH within 4 to 5 hrs, the cyanide level dropped rapidly.
5. When preserved to pH 12 then adjusted back to the initial pH after 24 hours, the cyanide level stayed relatively the same.

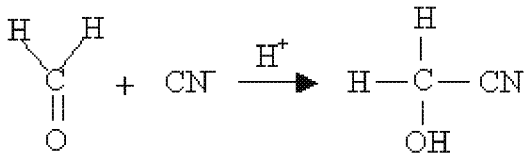
Based on the work presented here and on previous work of Pedersen et al. (1999), the cyanide formation pathway from glycine in the reaction of chloramination is proposed in pathway II.



Pathway II. Cyanide formation from chloramination of glycine (Pedersen et al., 1999).

Pathway II. Hand et al. (1983) proposed that glycine would decay to formaldehyde in the reaction with monochloramine. Formaldehyde reacts rapidly with monochloramine to form N-chloroaminomethanol (Pedersen et al., 1999). N-chloroaminomethanol reacts with formaldehyde to produce N-chlorodimethanolamine. The formation of N-chlorodimethanolamine is relatively slow and is catalyzed by OH^- that eventually leads to the formation of cyanide and CNCl. Therefore, at initial pH, there is no cyanide or CNCl being detected, since it is a base catalyzed reaction (Table 4 and 5).

Under chloramination conditions at pH >12, significant cyanide levels in Tables 3 to 6 indicate that cyanide is produced from the decay of N-chlorodimethanol under basic conditions. The addition of dechlorinating agent (sodium arsenite) before pH adjustment should prevent the occurrence of CNCl from the chlorination of cyanide, because cyanide is not produced until the pH is raised. Hence, CNCl and CNO should not be detected at pH 12 in any chloraminated sample. A significant increase in cyanide after 24 hours (Tables 4 and 5) indicates that the cyanide formation is a slow reaction that may take up to 24 hours to go completion. If the pH is adjusted back to its initial pH using hydrochloric acid within the first few hours, the produced cyanide and unreacted formaldehyde undergoes cyanohydrin formation (pathway III) and leads to a significant drop in cyanide, which is shown in Table 3. Once the cyanide generation is completed (after 24 hours), the cyanide level should remain relatively constant if the sample is stored at pH 12 for about 24 hours and then adjusted back to the initial pH (Table 3). This would indicate that there is no formaldehyde (or other aldehydes) remaining in solution after 24 hours, so there is no cyanohydrin formation consuming the produced cyanide; hence the cyanide level is stable.



Pathway III. Cyanohydrin formation (Morrison and Boyd, 1984)

CONCLUSIONS

Effluents from several wastewater treatment plants under chloramination conditions were examined, and cyanide levels were found to increase within the recommended holding times of the approved cyanide methods, if the samples were dechlorinated and preserved to pH 12. The sample preservation step is carried out to protect the sample integrity, and the analyte (cyanide) level should not change after preservative is added. The data indicates the presence of precursors that generate cyanide in these wastewater samples under strong basic conditions.

Significant differences were noted if disinfection is carried out under breakpoint chlorination conditions, rather than under chloramination conditions. Our experiments indicate that cyanide generation is completed almost immediately under breakpoint chlorination conditions. However, when using chloramination, cyanide generation is a slow reaction that may take up to 24 hours under highly basic conditions to go to completion. Once the cyanide reaction under chloramination conditions is complete, the cyanide level is stable and any changes in pH will not alter the cyanide level significantly.

Cyanide formation mechanisms for the reaction of glycine with free chlorine or chloramines are proposed. These mechanisms explain the differences that were observed in our experiments. All of the Districts' wastewater treatment facilities operate using chloramination, and no cyanogen chloride has been found in any of the effluents. However, our data shows that the existence of free chlorine in the disinfection process should lead to detectable cyanogen chloride formation. This phenomenon should be taken into consideration when breakpoint chlorination is being practiced.

We believe that amino acids are one of many possible precursors for cyanide formation, but the proposed mechanisms here do explain why we have seen cyanide in preserved samples, but not in samples that are analyzed immediately without pH adjustment.

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