Cyanide Generation During Preservation of Chlorinated Wastewater Effluent Samples for Total Cyanide Analysis

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ABSTRACT: Dechlorinating agents and pH adjustment are often used to preserve wastewater samples for cyanide analysis. The effects of four approved preservation protocols on the results of the total cyanide analysis of effluents from four Water Reclamation Plants (WRPs) were examined. The results differed widely, and a clear pattern emerged. Immediate analysis without pH adjustment generally gave total cyanide concentrations below the reporting limit of 5 µg/L, irrespective of the dechlorinating agents used. When the pH was adjusted to ≥ 12, a slight increase in the measured total cyanide concentration was observed when thiosulfate was used to dechlorinate the samples, and a significant increase (> 10 µg/L) was observed when arsenite was used as the dechlorinating agent. These results provide evidence that approved preservation protocols may give rise to cyanide formation in chlorinated wastewater effluent matrices.

KEYWORDS: cyanide, cyanide formation, wastewater treatment, preservation, pH, dechlorination, analytical methods, interference, analysis

INTRODUCTION AND BACKGROUND

Current scientific data indicate that cyanide can produce acute toxicity in aquatic organisms (Doudoroff, 1976; Doudoroff et al., 1966; Doudoroff et al., 1950; Doudoroff, 1956). Concentrations of cyanide above 5 µg/L can inhibit reproduction and reduce swimming performance in many fish and aquatic invertebrates (ATSDR, 1997). Other adverse effects include delayed mortality, disrupted respiration, and altered growth patterns. Because of these pronounced environmental impacts, the widespread detection

of cyanide in disinfected effluent continues to be a major concern for wastewater utilities and the focus of ongoing attention from regulatory entities. For example, the total cyanide discharge limits for several WRPs operated by the Sanitation Districts of Los Angeles County (Sanitation Districts) have been set at levels close to or below the current laboratory reporting limit of 5 μg/L. Wastewater treatment plants across the US have experienced difficulties meeting similarly low discharge limits for total cyanide (Kavanaugh et al., 2003).

In response to these challenges, a great deal of work has been undertaken to determine the source of the high cyanide measurements. Potential causes have been suggested: formation of cyanide during the treatment process, interferences related to the test procedure, or sample preservation protocols. Numerous wastewater treatment plants across the US have confirmed that high cyanide concentrations were occasionally found in chlorinated effluents despite the fact that the corresponding measurements on the influents were low (Deeb et al., 2003). In a study of the formation and fate of cyanide in the wastewater treatment processes, the Water Environment Research Foundation (WERF) examined cyanide levels using seven different analytical techniques at six different wastewater treatment plants across the US (Zheng et al., 2004d; Zheng et al., 2003). Occasional high levels were most often associated with chlorinated effluents, leading the authors to conclude that cyanide may be formed during disinfection (Kavanaugh et al., 2003).

Possible mechanisms for cyanide formation in the wastewater treatment processes have been identified in laboratory scale experiments. 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).

False positives or negatives caused by the analytical method or sample preservation protocols have been identified (Evans et al., 2003; Milosavljevic et al., 2005). Cyanide was formed in aqueous solutions when nitrites react with organic compounds (Rapean et al., 1980). Aromatic amines and glycine react with nitrite to form cyanide (Koshimizu et al., 1975). Such nitrite-reactive compounds are likely to be present in municipal wastewaters (Rapean et al., 1980). 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). If precursors that are amenable to nitration through condensative coupling reactions exist in disinfected effluents, as has been proposed (Rapean et al., 1980), it is possible that select preservation protocols could assist in cyanide-generating decomposition pathways (Weinberg et al., 2005). Using EPA method 335.3 (U.S. EPA, 1993) involving colorimetric analysis and UV digestion, the city of Hollywood, Florida reported significant differences in results from chlorinated final effluent, depending on the choice of dechlorinating agent used (Gulino et al., 2004); the City of San Jose concluded that cyanide is being generated after collection and during the preservation of plant effluent samples to which NaOH is added to adjust the pH to 12 (City of San Jose, 2004).

False positives resulting from cyanide formation during sample storage at high pH have very recently been reported by Weinberg, et al. (Weinberg et al., 2005). The authors indicated that the cyanide is being formed in the sample vials during storage and not in the original wastewater. However, removal of nitrite at the time of sample collection often prevented cyanide formation, confirming an earlier prediction by Carr et al. (Carr et al., 1997).

The Sanitation Districts' laboratories have carried out extensive studies on cyanide formation in samples from several wastewater treatment plants. The results of these studies corroborate findings elsewhere that total cyanide levels in primary influent and secondary effluent samples are generally below detection limits, but that detectable levels of total cyanide are frequently found in samples taken after chlorination of the secondary effluent. Additionally, our laboratories, along with other U.S. investigators, have seen indications suggesting the presence of an uncharacterized positive interference 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 been focused on the reliability of currently-accepted cyanide analytical methods.

The aforementioned methods suggest immediate analysis of samples. When immediate analysis is not possible, these methods require preservation by adjusting the samples to pH $\geq$ 12, using sodium hydroxide to retard the volatilization loss of $HCN_{(aq)}$ by converting it to the nonvolatile anion, CN^-. The methods all mandate the removal of residual chlorine through the addition of a dechlorinating agent. The study presented in this paper is focused on the effects that high pH preservation and the dechlorinating

agents have on the total cyanide results. The objective of this study was to determine how the total cyanide results are affected by different preservation procedures that are currently accepted by Standard Methods. Different dechlorinating agents and different conditions of pH adjustment were investigated to determine their effect on total cyanide results.

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) was 1 µg/L. The lowest point on the calibration curve (the minimum level or ML) was 5 µg/L; the reporting limit was 5 µg/L. An estimated value was reported for data that was between 1 and 5 µg/L. All samples were analyzed immediately, and the maximum time from sample collection until the start of the distillation was 15 minutes (APHA/AWWA/WEF, 1998). All samples taken for this study were chlorinated final effluent grab samples.

Sample Matrices. Wastewaters used in this study were collected from the final effluents of four tertiary WRPs operated by the Sanitation Districts. These plants were the San Jose Creek East Water Reclamation Plant (SJC East WRP), the San Jose Creek West Water Reclamation Plant (SJC West WRP), the Valencia Water Reclamation Plant (VAL WRP), and the Saugus Water Reclamation Plant (SAUG WRP). Average flows treated at these plants are 55, 29, 16, and 5.5 million gallons per day (MGD), respectively. All four plants are equipped with primary clarifiers, activated sludge process with biological nitrogen removal by nitrification and denitrification, final clarifiers, chlorination and

ammonia addition, granular media filters, chlorine contact tanks, and dechlorination with sulfur dioxide or sodium bisulfite before discharge to receiving water bodies.

Dechlorination and pH Adjustment

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).

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.

pH Adjustment When pH adjustment was required, the pH was measured using a calibrated pH meter and 50% NaOH solution was added to produce the desired pH. The ambient pH of the final effluents from treatment plants was approximately 7.4.

Experimental Design. In order to examine the effects of preservation steps on the total cyanide results, four preservation conditions were studied at each of the four treatment plants:

1. Sodium thiosulfate dechlorination and no pH adjustment
2. Sodium thiosulfate dechlorination with NaOH addition to pH=12.0 ± 0.1
3. Sodium arsenite dechlorination and no pH adjustment
4. Sodium arsenite dechlorination with NaOH addition to pH=12.0 ± 0.1

In order to investigate the variation of total cyanide levels during the day, chlorinated final effluent samples were collected throughout the day for periods of 4 to10 days at each of the four treatment plants.

RESULTS AND DISCUSSION

Tables 1 - 4 summarize the cyanide results for this study. Figures 1 - 4 illustrate the average of total cyanide results for the four preservation methods and show the general data trends.

Table 1 and Figure 1 show the total cyanide data for a period of ten days for SJC East WRP. Samples were collected hourly each day and a total of 242 samples were analyzed.

Table 2 and Figure 2 show the total cyanide data for a period of four days for SJC West WRP. Samples were collected hourly each day and a total of 104 samples were analyzed.

Table 3 and Figure 3 show the total cyanide data for a period of fifteen days for VAL WRP. Samples were collected at approximately two-hour intervals and a total of 166 samples were analyzed.

Table 4 and Figure 4 show the total cyanide data for a period of fourteen days for SAUG WRP. Samples were collected at 7 AM and 12 noon and a total of 154 samples were analyzed.

For samples dechlorinated with sodium thiosulfate:

1. With no pH adjustment, the total cyanide concentration in all of the 213 samples analyzed was below the reporting limit of 5 µg/L.

2. With pH adjustment to 12, 30 out of the 213 samples analyzed had total cyanide concentrations that were greater than or equal to the reporting limit; the results ranged from 5 µg/L to 18 µg/L. This preservation method has been routinely used for the Sanitation Districts' compliance samples and the pattern of sporadic

results higher than the reporting limit is consistent with the total cyanide data collected over the past few years. With a current discharge limit of 5.2 µg/L for Valencia WRP and future discharge limits of 4.1 or 4.2 µg/L for all seven WRPs, these positive results would result in discharge limit violations and non-compliance with NPDES discharge permits.

For samples dechlorinated with sodium arsenite:

1. With no pH adjustment, all but one of the 120 samples analyzed were below the reporting limit of 5 µg/L. These results were similar to those obtained from samples dechlorinated with sodium thiosulfate.

2. With pH adjustment to 12, 116 out of 120 samples analyzed had total cyanide concentrations that were well above the reporting limit of 5 µg/L. The results ranged from 5 µg/L to 37 µg/L with the majority of the values greater than 10 µg/L.

All of the individual results from all four WRPs for the four preservations methods tested are plotted in Figure 5.

CONCLUSIONS

When using immediate analysis without pH adjustment, the total cyanide levels in the final effluents of the four WRPs tested were below the reporting limit of 5 µg/L in all but one of over 300 samples tested (that one measurement was 6.3 µg/L). When the pH was adjusted to 12, higher total cyanide results were observed: when dechlorinated with thiosulfate, there were occasional total cyanide values above 5 µg/L; when dechlorinated with sodium arsenite, the total cyanide results were typically higher than 10 µg/L. These four preservation methods are recommended in Standard Methods, yet the total cyanide

results obtained using them were significantly different. This raises serious questions as to what the true cyanide concentration is in the effluent. Was cyanide actually present in the effluent or was cyanide formed in the sample during the preservation steps? Section 4500-CN-B of Standard Methods 20th Ed. states that " *Because most cyanides are very reactive and unstable, analyze samples as soon as possible. If sample cannot be analyzed immediately, add NaOH pellets or strong NaOH solution to raise sample pH to 12 to 12.5.*" The total cyanide results obtained from dechlorination and immediate analysis without pH adjustment most likely reflect the true total cyanide concentration. The data from this study show clearly that pH adjustment can significantly increase the total cyanide concentration in an effluent sample. Our data shows that total cyanide levels were below the reporting limit in four WRP effluents when pH was not adjusted. The mechanism of cyanide formation during sample preservation is unclear at the present time.

The relationship between high pH and the formation of cyanide in dechlorinated wastewater effluent is currently under investigation. Additional work is being planned to study the reaction mechanism.

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Table 1. Cyanide Results (in µg/L) for Preservation Study at SJC East WRP

Time	Description	Analysis Date									
		3/3/05	3/7/05	3/8/05	3/10/05	3/14/05	3/17/05	3/21/05	3/24/05	3/28/05	3/29/05
6:00 AM	Thio.	E 3.7	E 3.1	E 2.7	E 3.2	E 3.6	NA	E 2.6	E 3.8	E 2.7	E 3.5
	Thio. pH 12	5.6	E 4.6	E 4.9	E 4.6	6.3	NA	E 3.8	5.4	E 4.4	E 4.9
	Arsen.	NA	NA	NA	NA	E 3.3	NA	E 2.6	E 3.8	E 2.2	E 3.3
	Arsen. pH 12	NA	NA	NA	NA	20	NA	23	32	23	31
7:00 AM	Thio.	E 3.9	E 3.4	E 3.3	E 2.9	E 3.0	E 2.8	E 2.6	E 3.8	E 2.7	E 3.8
	Thio. pH 12	5.6	5.7	E 4.9	E 4.6	E 4.1	E 3.3	E 3.5	E 4.4	E 4.4	E 4.9
	Arsen.	NA	NA	NA	E 2.9	NA	E 2.8	E 2.6	E 4.1	E 3.0	E 3.5
	Arsen. pH 12	NA	NA	NA	26	NA	31	20	37	15	16
8:00 AM	Thio.	E 3.1	E 2.6	E 3.0	E 2.6	E 1.9	E 4.2	E 2.1	E 2.7	E 2.5	E 3.0
	Thio. pH 12	E 4.5	5.4	E 4.9	E 3.8	E 2.7	5.8	E 3.8	E 3.5	E 4.1	E 4.1
	Arsen.	NA	NA	NA	NA	E 2.7	E 4.2	NA	NA	NA	NA
	Arsen. pH 12	NA	NA	NA	NA	17	28	NA	NA	NA	NA
9:00 AM	Thio.	E 2.5	E 2.6	E 1.6	E 1.7	E 1.6	E 4.4	E 1.8	E 2.2	E 2.5	E 1.9
	Thio. pH 12	E 3.9	E 2.9	E 3.0	16	E 3.0	6.4	E 3.2	E 3.5	E 3.3	E 3.3
	Arsen.	NA	E 2.3	E 2.5	E 2.3	NA	NA	NA	NA	E 2.2	E 1.9
	Arsen. pH 12	NA	27	23	30	NA	NA	NA	NA	13	15
10:00 AM	Thio.	E 2.0	E 2.0	E 1.6	E 2.6	E 2.5	E 2.8	E 1.8	E 2.4	E 1.9	E 2.5
	Thio. pH 12	E 3.7	E 4.3	E 3.0	E 3.8	E 3.8	E 3.6	E 2.6	E 3.0	E 3.3	E 3.3
	Arsen.	NA	NA	E 2.5	NA	NA	E 2.8	E 2.1	E 2.4	E 2.5	E 2.2
	Arsen. pH 12	NA	NA	18	NA	NA	19	17	26	9.8	14
11:00 AM	Thio.	E 2.3	E 2.9	E 1.6	E 2.0	E 1.6	E 2.8	E 1.8	E 2.4	E 2.5	E 3.8
	Thio. pH 12	E 4.5	E 4.3	E 2.2	E 2.6	E 3.3	E 3.9	E 3.2	E 3.8	E 3.3	E 4.9
	Arsen.	NA	NA	E 2.2	E 3.5	NA	NA	NA	NA	NA	NA
	Arsen. pH 12	NA	NA	18	26	NA	NA	NA	NA	NA	NA
12:00 PM	Thio.	E 2.5	E 3.4	E 1.9	E 2.0	E 3.8	E 3.3	E 2.1	E 2.2	E 2.7	E 3.8
	Thio. pH 12	E 4.2	E 4.3	E 3.0	E 4.1	E 4.7	E 4.4	E 2.1	E 2.7	E 3.5	E 4.6
	Arsen.	NA	NA	NA	NA	NA	E 3.9	E 1.8	E 2.4	E 3.0	E 3.0
	Arsen. pH 12	NA	NA	NA	NA	NA	19	14	15	13	9.5
1:00 PM	Thio.	E 3.7	E 4.0	E 3.0	E 2.9	E 3.3	E 3.3	E 3.5	E 3.0	E 3.3	E 3.5
	Thio. pH 12	E 4.2	5.4	E 3.8	E 3.8	E 3.6	5.0	E 4.1	E 3.5	E 4.9	E 4.4
	Arsen.	NA	NA	NA	E 2.9	NA	NA	NA	NA	NA	NA
	Arsen. pH 12	NA	NA	NA	21	NA	NA	NA	NA	NA	NA
2:00 PM	Thio.	E 2.8	E 3.4	E 3.0	E 3.2	E 4.1	E 4.4	E 2.6	E 3.3	E 1.9	E 3.3
	Thio. pH 12	5.6	E 4.3	E 4.1	15	5.5	6.1	E 4.1	E 4.1	E 4.9	E 4.4

Notes:

Thio.	Dechlorinated with sodium thiosulfate, neutral pH
Thio. pH12	Dechlorinated with sodium thiosulfate, pH adjusted to 12 (+/-0.10) with 50% NaOH
Arsen.	Dechlorinated with 0.1N sodium arsenite, neutral pH
Arsen. pH12	Dechlorinated with 0.1N sodium arsenite, pH adjusted to 12 (+/-0.10) with 50% NaOH
Time:	Collection time of the samples
E:	Estimated values (between 1 µg/L and 5 µg/L)
NA:	Not Analyzed

Table 2. Cyanide Results (in µg/L) for Preservation Study at SJC West WRP

Time	Description	Analysis Date			
		4/4/05	4/5/05	4/6/05	4/7/05
6:00 AM	Thio.	E 1.6	E 1.1	E 1.7	E 2.9
	Thio. pH 12	E 4.1	E 2.5	E 3.1	E 4.3
	Arsen.	E 1.4	E 1.1	E 1.7	E 2.7
	Arsen. pH 12	18	17	18	10
7:00 AM	Thio.	E 2.2	E 1.1	E 1.7	E 2.4
	Thio. pH 12	E 3.8	E 2.7	E 3.4	E 4.3
	Arsen.	E 2.5	E 1.1	E 2.2	E 2.9
	Arsen. pH 12	13	14	11	8.3
8:00 AM	Thio.	E 1.9	E 1.4	E 2.0	E 2.3
	Thio. pH 12	E 4.6	E 2.5	E 3.6	E 4.3
9:00 AM	Thio.	E 2.2	E 1.1	E 2.0	E 2.4
	Thio. pH 12	E 4.4	E 2.5	E 3.9	E 3.7
10:00 AM	Thio.	E 1.9	E 1.4	E 1.7	E 2.4
	Thio. pH 12	E 3.3	E 2.5	E 3.6	E 3.5
	Arsen.	E 2.2	E 1.4	E 2.0	E 2.4
	Arsen. pH 12	18	12	16	11
11:00 AM	Thio.	E 1.6	E 1.4	E 1.1	E 1.9
	Thio. pH 12	E 2.7	E 2.7	E 2.5	E 2.7
12:00 PM	Thio.	E 1.6	E 1.1	E 3.4	E 1.6
	Thio. pH 12	E 3.5	E 2.2	5.6	E 2.9
	Arsen.	E 1.4	E 1.4	E 3.6	E 1.9
	Arsen. pH 12	18	12	14	8.0
1:00 PM	Thio.	E 1.6	E 1.4	E 3.4	E 1.6
	Thio. pH 12	E 2.7	E 2.5	E 4.7	E 2.7
2:00 PM	Thio.	E 1.1	E 1.6	E 2.2	E 1.3
	Thio. pH 12	E 3.0	E 3.0	E 3.6	E 2.7

Notes:

Thio.	Dechlorinated with sodium thiosulfate, neutral pH
Thio. pH12	Dechlorinated with sodium thiosulfate, pH adjusted to 12 (+/-0.10) with 50% NaOH
Arsen.	Dechlorinated with 0.1N sodium arsenite, neutral pH
Arsen. pH12	Dechlorinated with 0.1N sodium arsenite, pH adjusted to 12 (+/-0.10) with 50% NaOH
Time:	Collection time of the samples
E:	Estimated values (between 1 µg/L and 5 µg/L)

Table 3. Cyanide Results (in µg/L) for Preservation Study at Valencia WRP

Time	Description	Analysis Date														
		5/16	5/17	5/18	5/19	5/23	5/24	5/25	5/26	6/1	6/2	6/7	6/9	6/13	6/14	6/16
6:30 AM	Thio.	n.d.	E 1.8	E 2.5	E 1.9	E 1.5	n.d.	n.d.	n.d.	NA	NA	n.d.	E 1.7	n.d.	n.d.	n.d.
	Thio. pH 12	E 4.4	E 2.2	5.0	E 2.2	6.4	E 1.7	E 2.8	E 4.3	NA	NA	E 4.0	E 2.3	E 1.4	E 1.1	n.d.
	Arsen.	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	n.d.	E 1.4	E 2.9	n.d.	n.d.
	Arsen. pH 12	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	13	15	11	11	16
7:00 AM	Thio.	E 4.1	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA
	Thio. pH 12	E 1.1	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA
	Arsen.	E 3.3	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA
	Arsen. pH 12	14	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA
9:00 AM	Thio.	E 2.2	E 1.5	E 2.2	E 2.5	n.d.	n.d.	n.d.	n.d.	E 1.4	E 2.3	n.d.	E 2.0	E 1.7	n.d.	n.d.
	Thio. pH 12	E 2.7	8.0	E 3.6	E 3.3	E 3.2	E 2.5	E 4.2	E 2.0	E 3.1	E 4.0	E 2.9	E 2.5	E 1.7	n.d.	n.d.
	Arsen.	E 1.9	E 3.7	E 2.5	E 2.5	E 2.3	n.d.	n.d.	E 1.7	E 2.0	E 3.4	E 2.3	E 2.8	E 1.7	n.d.	n.d.
	Arsen. pH 12	11	11	12	12	13	E 4.4	12	14	13	17	16	20	14	21	11
9:30 AM	Thio.	n.d.	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA
	Thio. pH 12	E 1.9	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA
11:30 AM	Thio.	E 2.4	E 3.7	E 2.0	E 3.6	n.d.	n.d.	E 1.1	n.d.	E 2.2	E 2.3	n.d.	E 1.4	n.d.	E 1.1	n.d.
	Thio. pH 12	E 2.2	6.2	7.0	E 4.4	E 2.0	E 3.9	E 2.0	E 1.4	E 3.9	E 3.1	E 1.4	8.8	E 1.1	E 2.3	n.d.
	Arsen.	6.3	E 3.1	E 3.4	E 3.0	E 1.5	E 2.2	E 1.7	E 1.1	E 2.2	E 3.7	E 1.1	E 2.5	n.d.	E 2.9	E 2.9
	Arsen. pH 12	14	9.6	12	12	9.3	13	14	18	13	18	13	18	19	17	14
Noon	Thio.	E 1.1	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA
	Thio. pH 12	8.4	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA
	Arsen.	E 3.0	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA
	Arsen. pH 12	14	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA

Notes:

Thio.	Dechlorinated with sodium thiosulfate, neutral pH
Thio. pH12	Dechlorinated with sodium thiosulfate, pH adjusted to 12 (+/-0.10) with 50% NaOH
Arsen.	Dechlorinated with 0.1N sodium arsenite, neutral pH
Arsen. pH12	Dechlorinated with 0.1N sodium arsenite, pH adjusted to 12 (+/-0.10) with 50% NaOH
Time:	Collection time of the samples
E:	Estimated values (between 1 µg/L and 5 µg/L)
NA:	Not Analyzed
n.d.	Not detected (< 1.0 µg/L)

Table 4. Cyanide Results (in µg/L) for Preservation Study at Saugus WRP

Time	Description	Analysis Date													
		5/17	5/18	5/19	5/23	5/24	5/25	5/26	6/1	6/2	6/7	6/9	6/13	6/14	6/16
7:00 - 7:30 AM	Thio.	n.d.	n.d.	E 1.1	n.d.	n.d.	n.d.	E 2.0	n.d.	E 2.0	n.d.	E 1.4	n.d.	n.d.	n.d.
	Thio. pH 12	18	E 2.8	E 3.3	E 2.3	E 3.6	E 2.8	6.6	E 2.5	E 4.5	E 3.7	E 1.1	n.d.	E 1.1	n.d.
	Arsen.	E 2.8	E 3.1	E 1.4	n.d.	n.d.	E 1.1	E 1.4	E 2.2	E 4.0	E 1.1	E 1.7	n.d.	n.d.	n.d.
	Arsen. pH 12	12	8.7	6.1	E 4.4	5.3	13	10	5.6	7.1	7.8	12.7	9.2	9.4	8.0
9:30 - 10 AM	Thio.	n.d.	E 1.4	n.d.	n.d.	E 1.4	n.d.	E 1.1	E 1.1	E 1.1	n.d.	n.d.	n.d.	n.d.	n.d.
	Thio. pH 12	E 2.8	11	E 1.1	E 1.5	E 2.8	E 2.0	E 4.0	E 3.1	E 2.6	E 1.7	6.2	n.d.	n.d.	n.d.
	Arsen.	NA	NA	NA	NA	NA	NA	NA	E 3.1	E 4.0	E 2.0	E 3.1	E 1.1	n.d.	n.d.
	Arsen. pH 12	NA	NA	NA	NA	NA	NA	NA	6.4	9.6	7.8	6.2	E 3.4	7.2	7.7
12 - 12:30 PM	Thio.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	E 2.2	E 1.4	E 2.6	E 1.1	n.d.	n.d.	n.d.
	Thio. pH 12	8.3	E 1.4	E 1.1	E 1.2	E 1.9	E 1.4	E 2.6	5.0	E 4.0	E 3.4	5.7	E 1.1	n.d.	n.d.
	Arsen.	E 1.2	E 2.5	n.d.	n.d.	n.d.	n.d.	E 2.0	E 3.3	E 2.6	E 2.9	E 3.7	n.d.	n.d.	n.d.
	Arsen. pH 12	13	12	6.4	7.3	7.8	13	5.4	7.2	7.7	7.8	13.6	8.0	E 4.3	12.6

Notes:

Thio.	Dechlorinated with sodium thiosulfate, neutral pH
Thio. pH12	Dechlorinated with sodium thiosulfate, pH adjusted to 12 (+/-0.10) with 50% NaOH
Arsen.	Dechlorinated with 0.1N sodium arsenite, neutral pH
Arsen. pH12	Dechlorinated with 0.1N sodium arsenite, pH adjusted to 12 (+/-0.10) with 50% NaOH
Time:	Collection time of the samples in May were 7 AM, 9:30 AM, and 12 PM, and in June they were 7:30 AM, 10 AM, and 12:30 PM
E:	Estimated values (between 1 µg/L and 5 µg/L)
NA:	Not Analyzed
n.d.	Not detected (< 1.0 µg/L)

Figure 1

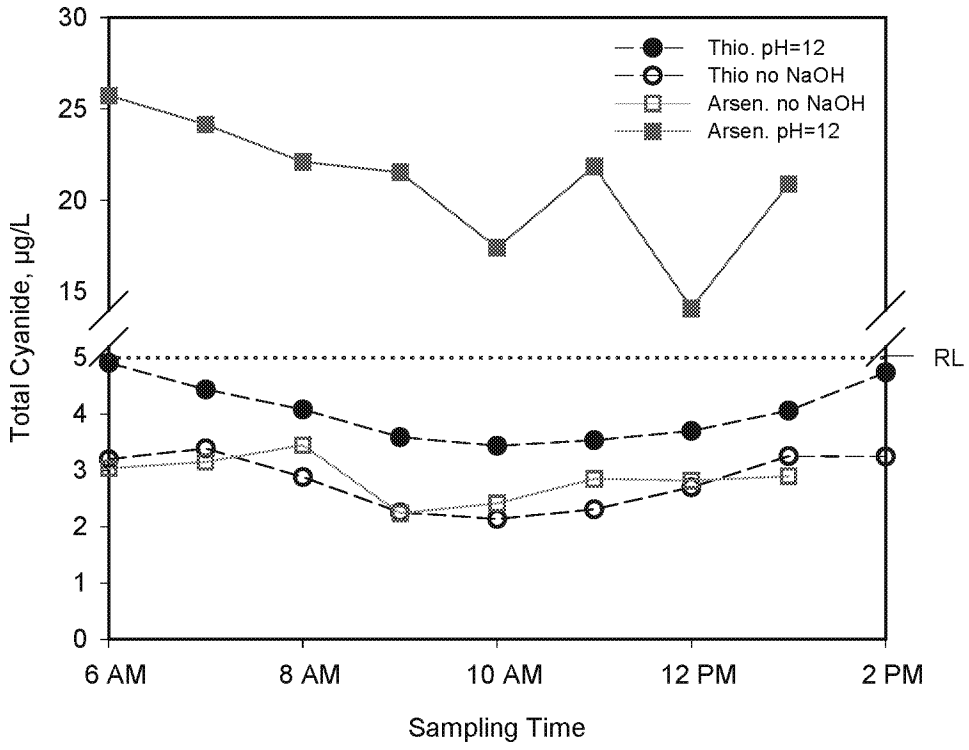
Thio. pH=12
Thio no NaOH
Arsen. no NaOH
Arsen. pH=12
RL
Total Cyanide, µg/L
30
25
20
15
5
4
3
2
1
0
6 AM
8 AM
10 AM
12 PM
2 PM
Sampling Time

Figure 2

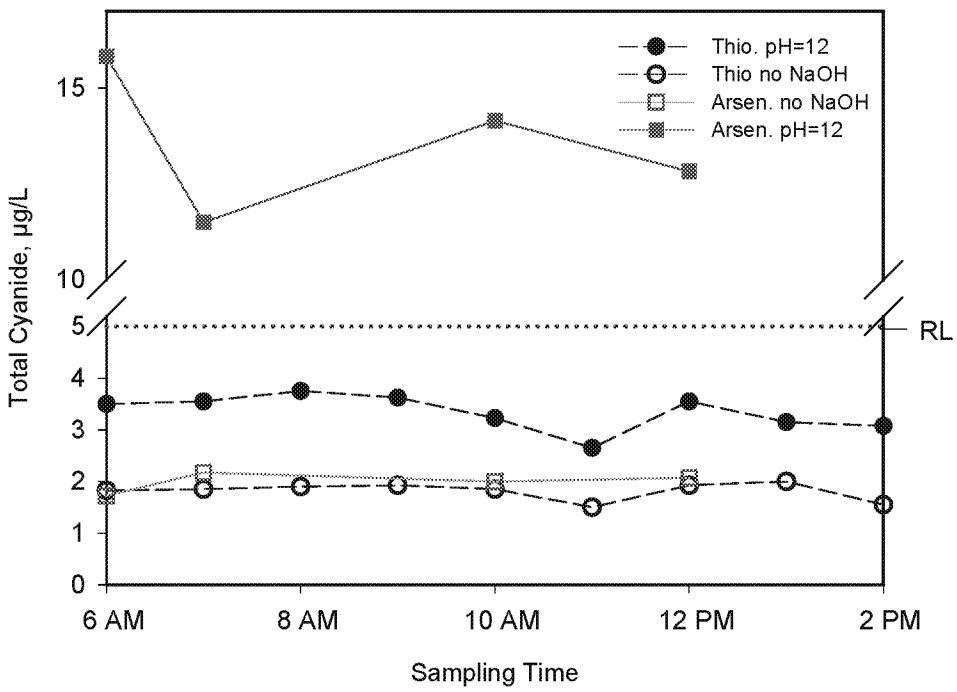
Thio. pH=12
Thio no NaOH
Arsen. no NaOH
Arsen. pH=12
RL
Total Cyanide, µg/L
15
10
5
4
3
2
1
0
6 AM
8 AM
10 AM
12 PM
2 PM
Sampling Time

Figure 3

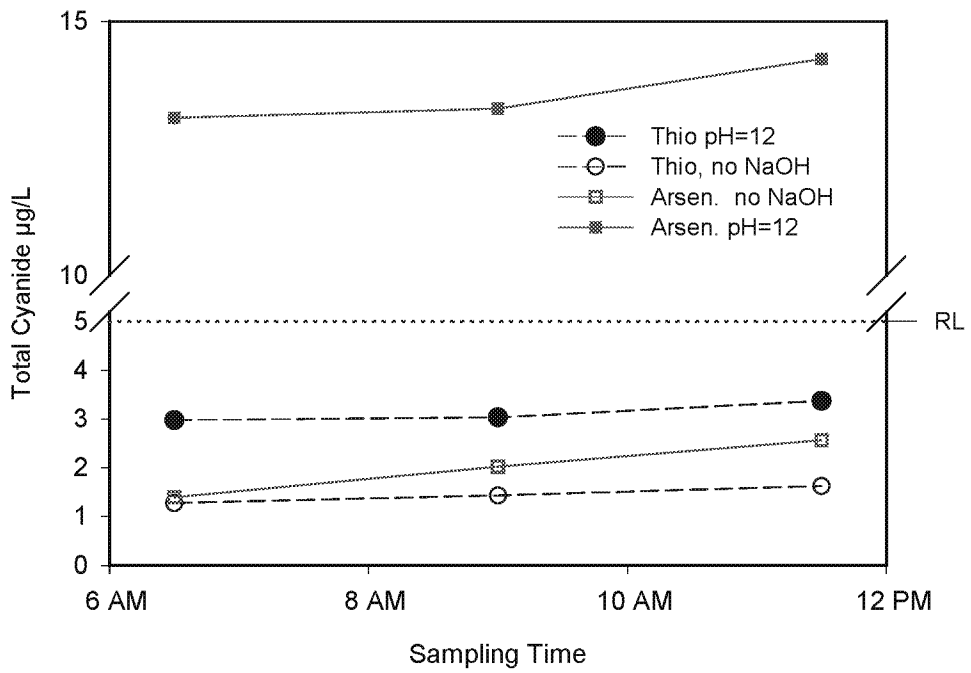
15
10
5
4
3
2
1
0
Total Cyanide µg/L
Thio pH=12
Thio, no NaOH
Arsen. no NaOH
Arsen. pH=12
RL
6 AM
8 AM
10 AM
12 PM
Sampling Time

Figure 4

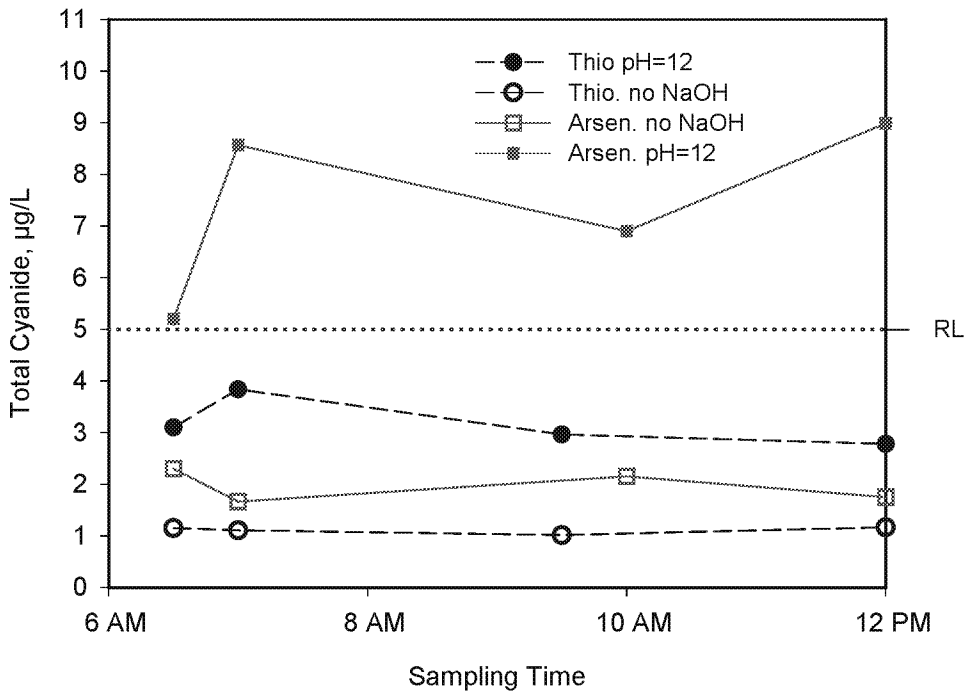
Thio pH=12
Thio. no NaOH
Arsen. no NaOH
Arsen. pH=12
RL
Total Cyanide, µg/L
0
1
2
3
4
5
6
7
8
9
10
11
6 AM
8 AM
10 AM
12 PM
Sampling Time

Figure 5

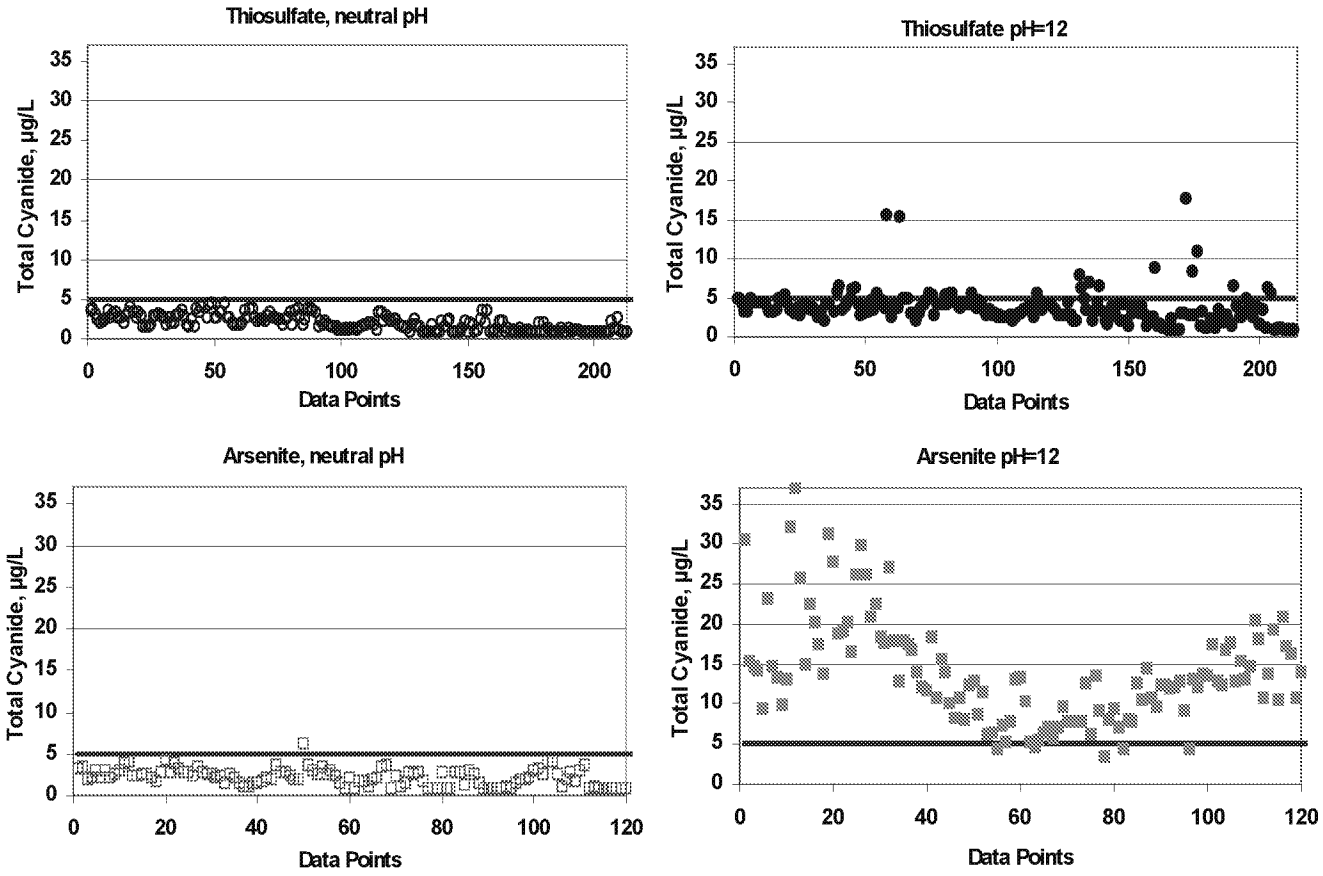
Thiosulfate, neutral pH
Total Cyanide, µg/L
Data Points
Thiosulfate pH=12
Total Cyanide, µg/L
Data Points
Arsenite, neutral pH
Total Cyanide, µg/L
Data Points
Arsenite pH=12
Total Cyanide, µg/L
Data Points

Figure Captions

Figure 1 Total Cyanide Results for Preservation Study at SJC East WRP. Each point represents a 10-day average. Data below the reporting limit (RL line) are estimated values.

Figure 2 Total Cyanide Results for Preservation Study at SJC West WRP. Each point represents a 4-day average. Data below the reporting limit (RL line) are estimated values.

Figure 3 Total Cyanide Results for Preservation Study at Valencia WRP. Each point represents an 15-day average. Data below the reporting limit (RL line) are estimated values.

Figure 4 Cyanide Results for Preservation Study at Saugus WRP. Each point represents a 14-day average. Data below the reporting limit (RL line) are estimated values.

Figure 5 Results for Four Approved Preservation Methods Compiled from all WRPs