Cyanide Concentration Changes in Environmental Water Samples as a Function of Sample Preservation and Holding Time

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Section 1. Introduction

Most cyanide analysis sampling protocols specify preservation of samples at a pH of 12 or higher. Sample preservation is intended to minimize changes in analyte concentration to allow sample storage for up to 14 days prior to analysis. The source of a water sample, sample pre-treatment, and the presence of possible matrix interferences must also be considered in determining appropriate sampling and preservation procedures to avoid unintentional formation or destruction of cyanide species.

Matrix interferences can cause either negative or positive analytical biases depending upon the composition of the sample being tested. The species of cyanide present in a sample is directly affected by the pH, and presence of; oxidizers, sulfur or sulfur compounds, and transition metals. **Table 1** provides a summary of cyanide analysis interferences associated with sampling, preservation, and storage.

The U.S. EPA is aware of problems related to sampling and preservation practices and has recently taken steps to address these problems. ASTM D 7365-09a Standard Practice for Sampling, Preservation, and Mitigating Interferences in Water Samples for Analysis of Cyanide(1) was included in the U.S. EPA Method Update Rule (MUR) of September 23, 2010 (2) applicable to 40 CFR 136 Clean Water Act methods for testing of wastewater samples.

This poster presents data demonstrating decreases and increases in total and available cyanide concentration in samples as a function of the metals present, treatment chemicals added, and pH.

Compound	Description of Interferences
Residual chlorine, peroxide, or other oxidizers	React with cyanide in solution, rapidly decreasing the cyanide concentration. Oxidizers can co-exist with cyanide.
Chloramines	React with sample at pH>10, increasing the cyanide concentration.
Sulfide	Reacts with cyanide to form thiocyanate, decreasing the cyanide concentration. Reaction is especially rapid if metal sulfides, such as lead sulfide, are present. The reaction is fairly slow without metal sulfides.
Native Sulfur (colloidal sulfur)	Reacts with cyanide to form thiocyanate, decreasing the cyanide concentration. Reaction is very fast with colloidal sulfur.
Sulfite	Reacts with strong cyanide complexes at pH>10, decreasing the cyanide concentration. The reaction is almost immediate at pH>12.
Light (<350nm)	Reacts with strong metal-cyanide complexes, releasing free cyanide.
Ascorbic acid	Reacts with cyanide, decreasing the cyanide concentration. Sample holding time when ascorbic acid is added is less than 48 hours. In some samples, ascorbic acid can react with ammonia or other nitrogen sources and increase the cyanide concentration.
Formaldehyde	Reacts with cyanide, decreasing the concentration. In some samples, formaldehyde reacts with ammonia or other nitrogen sources and increases the cyanide concentrations.

Table 1. Cyanide Interferences

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Section 2. Experimental

Oxidants

To illustrate the effect of oxidants, three synthetic wastewater matrices containing 20-mg/L thiocyanate (SCN⁻) and 10 mg/L Nitrate Nitrogen ($NO_{2}^{-}N$) were treated with hypochlorite (CIO), hydrogen peroxide (H_2O_2), and ascorbic acid (commonly used as a dechlorination agent during sampling) at 0.5 mg/L each. An identical matrix without oxidizer was also prepared. Each solution was adjusted to pH 12 with sodium hydroxide (NaOH) and analyzed for available cyanide (without ligand addition) using an OI Analytical FS3700 system configured with an OIA 1677 Available Cyanide cartridge. Samples were stored at room temperature, in the dark. The results of this study are shown in **Figure 1**.



The control matrix contained only trace cyanide (0.2-0.3 ppb) while the addition of oxidant generated cyanide almost immediately. Cyanide formation continued throughout the entire two days of the test. The amount of cyanide generation is greater with hypochlorite than with peroxide. Even the control sample, the synthetic matrix adjusted to pH 12, generated trace cyanide during the 48-hour test. The ascorbic acid containing solution, generated cyanide immediately after NaOH addition, then decreased with cyanide over time. **Figure 2**, illustrates the rapid loss of cyanide in samples containing ascorbic acid and adjusted to pH 12.

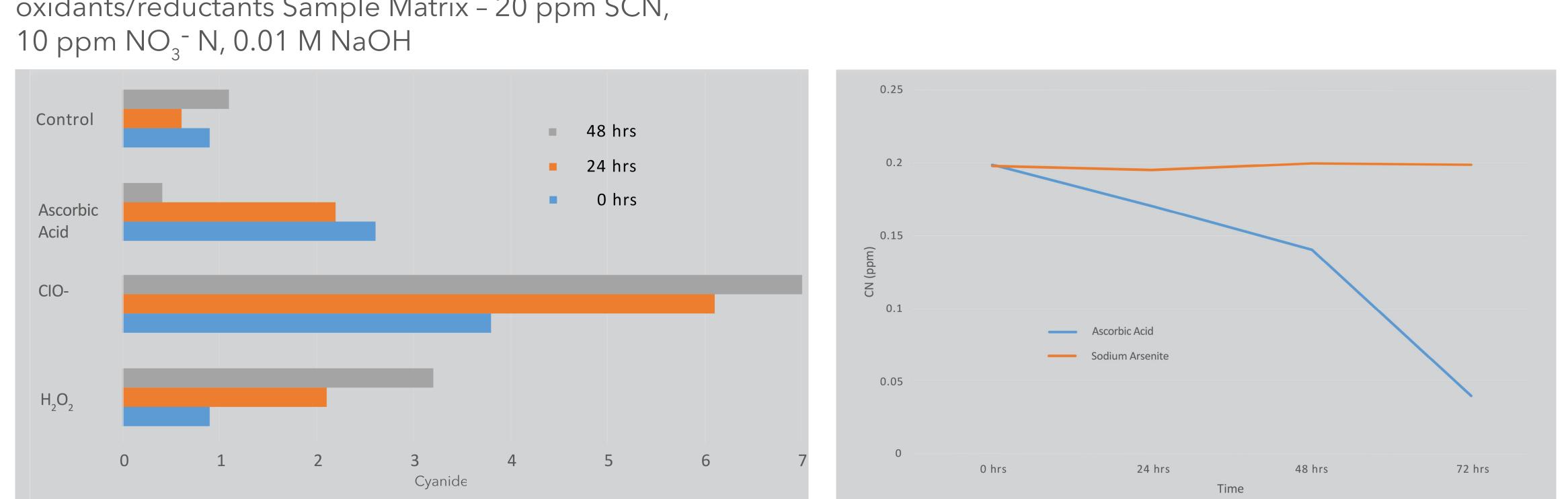
Sulfite

Reducing agents, such as ascorbic acid and sodium thiosulfate, are often recommended to dechlorinate samples during sample collection. Then, sample pH is adjusted to pH 12 with NaOH for storage, up to 14 days before analysis. A negative bias by distillation of samples containing thiosulfate has been demonstrated previously. Many municipalities use sodium sulfite, or sulfur dioxide, to dechlorinate wastewater streams prior to discharge. Preservation of sulfite containing samples at pH 12 with NaOH results in rapid loss of cyanide concentration. According to the data in Figure 3, cyanide samples that have been treated with sulfites should not be preserved to pH 12 prior to analysis.

While data suggests that low level cyanide test samples should not be adjusted to pH 12 prior to analysis, holding time studies should be conducted on each matrix to confirm that cyanide will not be lost if samples are not pH adjusted. For example (see **Figure 4**), an ASTM D 6888 cyanide holding time study of non-preserved samples lost cyanide within a few days for some samples, while cyanide concentrations seemed to remain stable for other matrices.

These same samples obtained quantitative recovery on portions that were adjusted to pH 12 prior to analysis (Figure 5). The surface water sample decreased in available cyanide (Figure 4), yet obtained the correct result when analyzed for total cyanide (indicating that cyanide is slowly being "bound" to the ferrous iron present in the sample).

Figure 1. Generation of cyanide at pH 12 with various oxidants/reductants Sample Matrix - 20 ppm SCN,



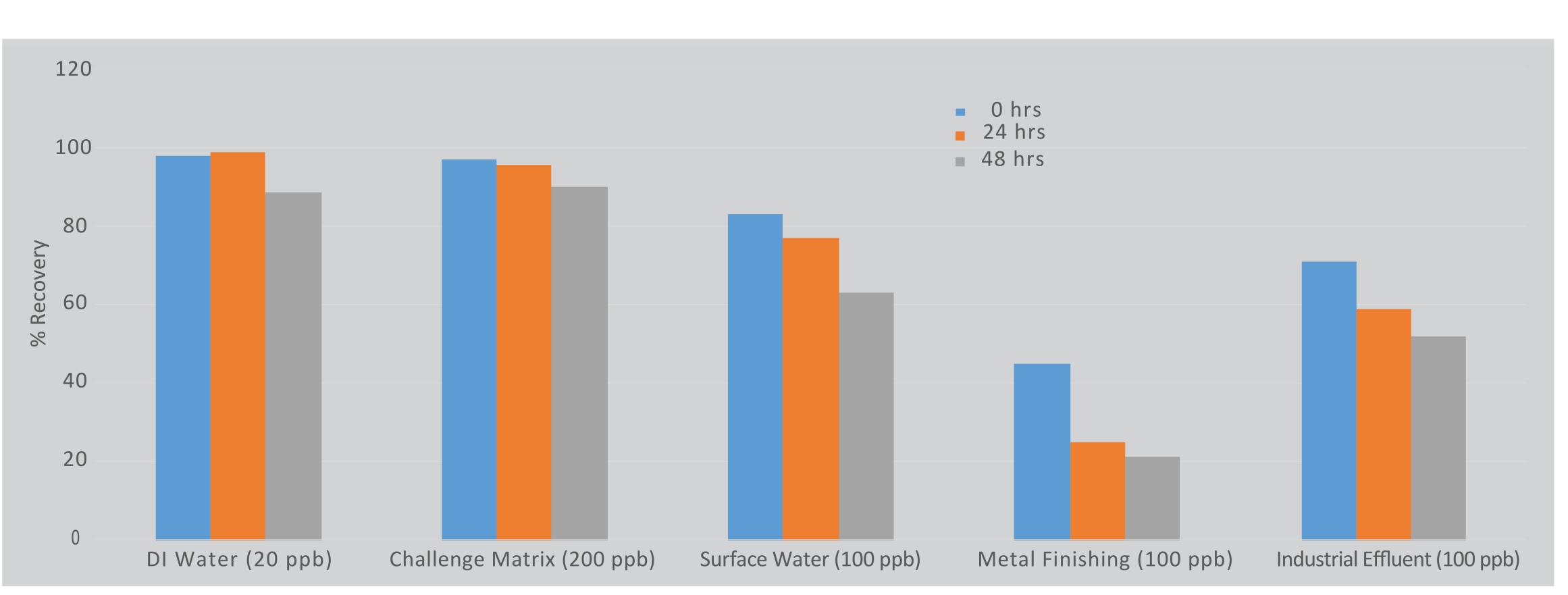


Figure 4. Holding Time Study on "As Received" Samples, (no NaOH added)

Figure 2. Loss of cyanide with ascorbic acid at pH 12 Figure 3. Cyanide loss in samples containing sulfite

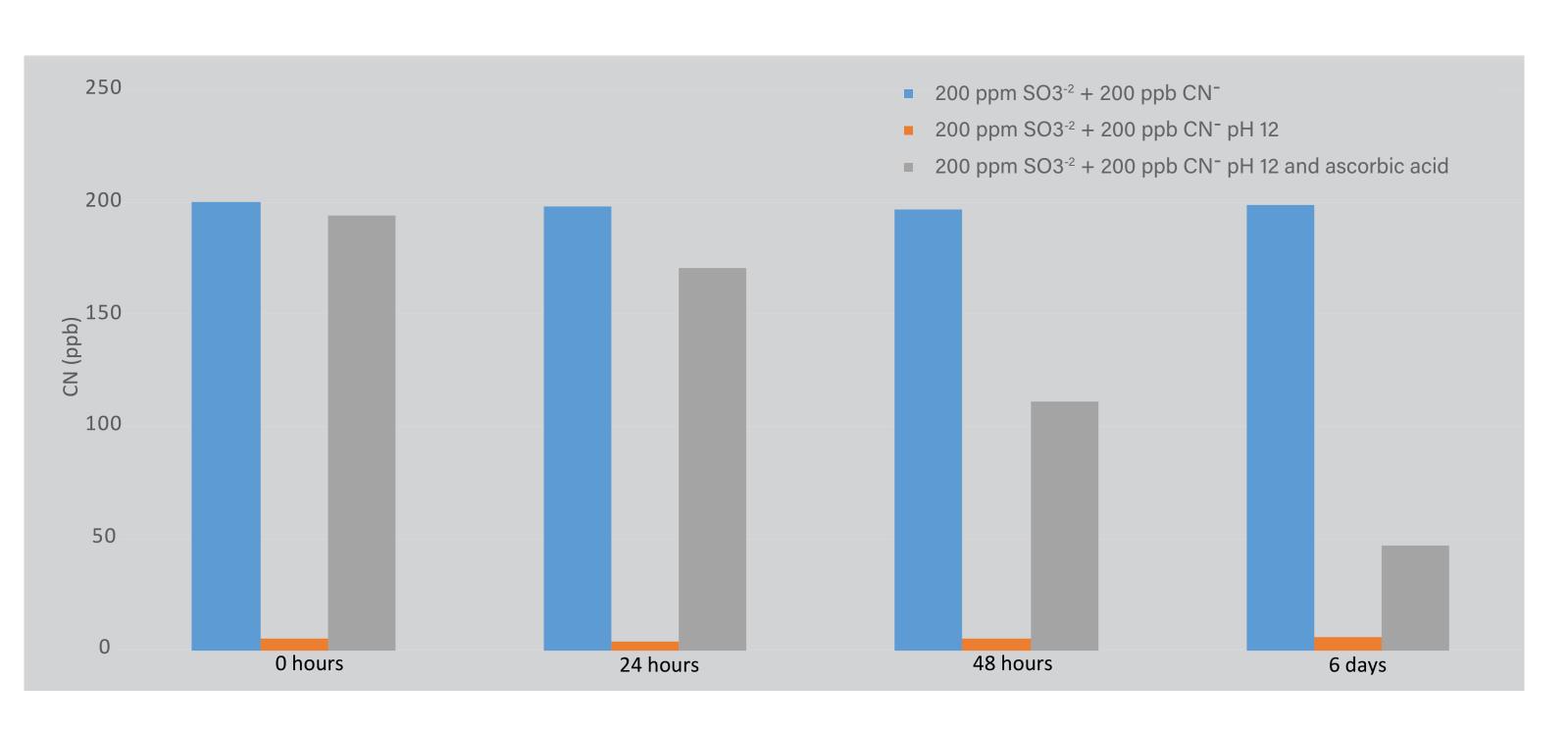
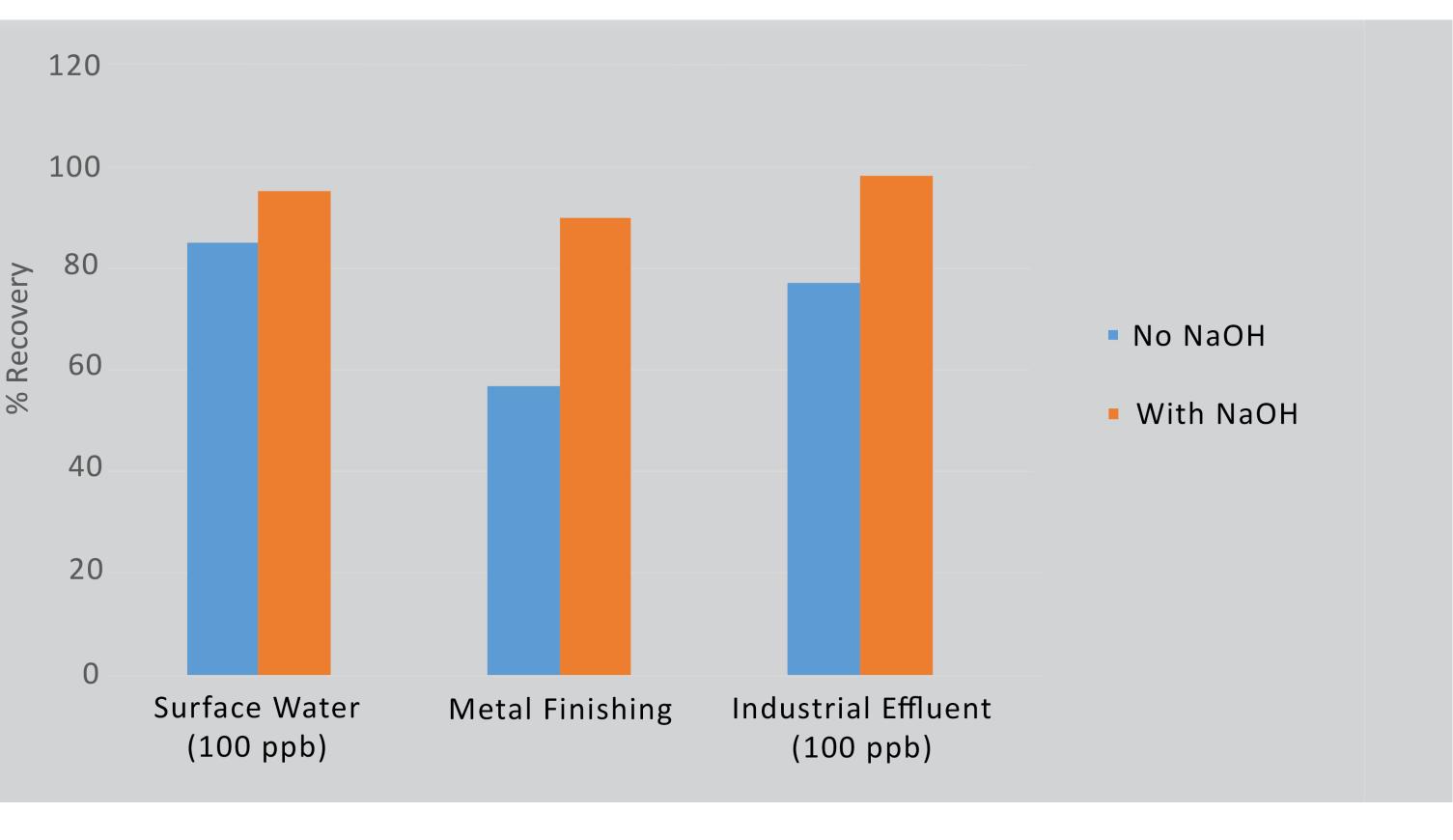


Figure 5. Comparison of Holding Time on Cyanide Recovery with and without NaOH Added



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Section 3. Conclusions

ASTM D 7365-09a Standard Practice for Sampling, Preservation and Mitigating Interferences in Water Samples for Analysis of Cyanide was included in the U.S. EPA Method Update Rule (MUR) of September 23, 2010 (2) applicable to 40 CFR 136 Clean Water Act methods for testing of wastewater samples.

This standard describes procedures for preservation of samples and warns that pH adjustment could result in the generation of cyanide in concentrations high enough to exceed NPDES permits. Formation of cyanide in sodium hydroxide preserved synthetic matrices containing contaminants that are likely to be present in natural waters was confirmed. Data presented also demonstrates cyanide loss as a result of pH adjustment. While this data suggests cyanide samples should not be preserved at an elevated pH, other data demonstrated that without pH adjustment cyanide results could be too low. When in doubt, samples should be processed immediately, or within minutes, after collection.

Section 4. References

- 1. ASTM D 7365-09a, "Standard Practice for Sampling," Preservation and Mitigating Interferences in Water Samples for Analysis of Cyanide", ASTM International, West Conshohocken, PA, www.astm.org.
- 2. Federal Register, Vol. 75, No. 184, September 23, 2010, Guidelines for Establishing Test Procedures for Analysis of Pollutants Under the Clean Water Act; Analysis and Sampling Procedures; Proposed Rule, http://edocket. access.gov/2010/pdf/2010-20018.pdf.



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