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Cyanide analysis in wastewater

Heather Marie Lutes

CYANIDE ANALYSIS IN WASTEWATER

A Project

Presented to the

Faculty of

California State University,

San Bernardino

In Partial Fulfillment

of the Requirements for the Degree

Master of Science

in

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Approved by:

[redacted]

Dr. Brett Stanley, Chair, Chemistry

8/12/09

Date

[redacted]

Dr. James Noblet

[redacted]

Dr. Robert Phalen, Health Science
And Human Ecology

ABSTRACT

Wastewater treatment plants in the Santa Ana Watershed are having difficulties analyzing and detecting cyanide in their wastewater. There are inconsistent results in the methods currently being used. The objective of this project is to help them find a uniform method in which to detect cyanide free of the inconsistencies they currently see. Influent and effluent wastewater samples from various wastewater treatment plants were used to evaluate analytical methods that are based on United States Environmental Protection Agency (U.S. EPA) method 335.2, Standard Method 4500, and QuikChem method 10-204-99-1-X. Colorimetric free and total cyanide methods and amperometric free and available cyanide methods were analyzed. A number of conditions used in sample treatment and analysis were examined including: distillation, macro distillation versus micro distillation, preservation with sodium hydroxide, sulfide treatment with lead carbonate, and chlorination/dechlorination. The data suggests that distillation removes contaminants or interferences as a variable and that micro distillation yields better cyanide recoveries than macro distillation. Preserving samples with sodium hydroxide increases the levels of cyanide

detected in the samples. The level of cyanide detected in a sample is higher with a preserved sample that has been treated with chlorination and dechlorination compared to a preserved sample that has not been. Treating the samples for sulfide interference with lead carbonate leads to higher amounts of cyanide detected in the wastewater samples. Further samples need to be analyzed to determine statistically if these inferences are correct in order to determine a uniform method for cyanide analysis.

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DEDICATION

To my mom and my dad who have always been there for me.

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INTRODUCTION

Purpose of the Project

Cyanide is proving to be very difficult to analyze for wastewater treatment plants (WWTPs) in the Santa Ana Watershed. The purpose of this project was to look at and determine the methods that would best prevent the occurrence of false readings during testing and analysis of cyanide in wastewater. This project was designed to help those WWTPs in the Santa Ana Watershed who are in the process of developing a uniform method that minimizes or eliminates interferences.

The Santa Ana Watershed

Eastern Municipal District, Inland Empire Utilities Agency, Orange County Water District, San Bernardino Valley Municipal Water District, and Western Municipal Water District all are members of the Santa Ana Watershed Project Authority (SAWPA). The WWTPs that are up-stream dischargers to the Santa Ana River are members of the Santa Ana River Dischargers Association (SARDA). Both organizations are dedicated to working together to ensure

that the Santa Ana Watershed is economically and environmentally vital for those living there. The Santa Ana Watershed is located in Southern California and incorporates parts of Riverside, Los Angeles, Orange, and San Bernardino Counties. It encompasses an area of approximately 2,800 square miles. Water from the counties listed above flow into this watershed *(1)*.

Classification of Cyanide

The United States Environmental Protection Agency (U.S. EPA) acknowledges "cyanide or cyanides…as the group of simple and complex chemical compounds that can be determined as (a) cyanide ion (CN^-)" *(2)*. The chemical composition is a function of the pH, temperature, and trace metal content in the wastewater *(3)*. Cyanide may be classified as free, total, or available depending on characteristics of the compound and the water it resides in.

Free Cyanide

Cyanide ions and hydrogen cyanide (HCN) are commonly referred to as free cyanide. However, the U.S. EPA does not limit the definition of free cyanide to just cyanide ions and hydrogen cyanide; they consider any cyanide

species that will readily dissociate into free form as free cyanide *(4)*. The proportion of cyanide ions to hydrogen cyanide in wastewater is dependent on the pH of the solution. When the pH is between 9.1 and 9.3 the CN^- and HCN are in equilibrium and are equally represented in solution. When the pH is at 11 plus or minus 0.2, 99% of the cyanide exists as CN^-. When the pH is at 7 plus or minus 0.2, 99% of the cyanide exists as HCN *(3)*.

Available Cyanide

Free cyanide can be referred to as available cyanide when weak metal complexes dissociate easily at low concentrations in wastewater samples. Even though metal-cyanide complexes alone are not as toxic as free cyanide, when they dissociate they release free cyanide and a metal cation that can be toxic as well *(3)*. Inevitably, most cyanide in water will form hydrogen cyanide and evaporate into the atmosphere. However, enough stays behind to create a serious environmental problem because it could potentially contaminate groundwater. This is because at high enough levels cyanide becomes toxic to the micro-organisms that are breaking it down in the soil; therefore cyanide is able to persist long enough to pass through the soil and into groundwater *(5)*.

Total Cyanide

When wastewater samples are analyzed the concentrations of cyanide found in them are collectively referred to as total cyanide (TCN). TCN is the free cyanide that is present in a sample after dissociating the complex metal cyanides by persulfate digestion *(6)*. When analyzing wastewater all the cyanide detected in the sample is referred to as TCN because it is hard to distinguish between the different cyanide complexes. However, the U.S. EPA recognizes that a distinction needs to be made between the bio-available and extremely toxic free cyanide and TCN which encompasses all forms of cyanide *(7)*.

Sources of Cyanide

Cyanide is released and formed in aqueous environments by both industrial operations and natural means. Industrial operations include: "electroplating, electronics manufacturing, precious metal extractions, pharmaceutical production, blast furnaces, petroleum refineries, and coke producing plants" *(8)*. Naturally occurring cyanide is found in tapioca, lima beans, almonds, and the pits or seeds of common fruit such as apricots, apples, and peaches *(5)*.

Toxicity of Cyanide

Today many pollutants exist that are threatening the health and sustainability of the environment and living beings who reside there. The attention that environmental regulatory agencies give these pollutants depends in part on the toxicity of them. As a class, cyanide is one of the toxic pollutants that the U.S. EPA is concerned with. Cyanide ions form a stable complex by acting as a ligand and binding with metal ions such as cadmium, lead, nickel, zinc, or iron. The level of stability that a cyanide complex has is determined by the type of metal it binds to and its oxidation state. The more stable the compound the less toxic it is. Most metal-binding cyanide complexes are relatively stable and as a result are less toxic to the environment *(7)*. The unstable, toxic cyanide compounds that the U.S. EPA is concerned with are non-binding cyanide ions (CN^-) and those that bind with hydrogen to form hydrogen cyanide (HCN) *(4)*. Free Cyanide is the only form of cyanide regulated by the U.S. EPA because of its availability in wastewater and its toxic nature. As a result, analytical methods for free or available cyanide detection are preferred over the methods for total cyanide detection.

Health Effects

Free cyanide that is released into the environment has serious impacts on the health and well being of those that reside there *(7)*. As mentioned previously cyanide complexes have different toxicity levels affecting life in many different ways. The effect of these toxicity levels on living-beings depends on the dose and length of exposure. The impacts of cyanide in the environment are not limited exclusively to humans. Aquatic life that resides in cyanide polluted water can be impacted more than humans. Studies show that cyanide is 1000 times more toxic to aquatic life than to humans *(9)*. Even though the cyanide in water is not known to reside inside aquatic life tissues it still causes serious health problems for them *(5)*. Cyanide concentrations over 5 µg/L (ppb) inhibits reproduction and minimizes the swimming performance in fish and aquatic invertebrates. It has caused early death, respiration problems, and changes in the growth patterns of aquatic life *(10)*.

Cyanide poisoning symptoms in humans start with respiratory problems, followed by seizures, and can eventually lead to death if not treated. The speed at which this occurs inevitably depends on the route,

duration, concentration of exposure, and the vitality of the person exposed. However, the health effects seem to be independent of the route of exposure *(5)*. Most people exposed over a long period of time to low levels, or, a short period time to high levels of cyanide may have difficulty breathing, chest pain, vomiting, blood changes, headaches, and enlarged thyroid glands *(11)*. The effects of cyanide are slower when it is ingested through the skin. Skin exposure to hydrogen cyanide and cyanide salts often results in rashes and sores. While most people are not exposed to high enough levels to cause serious health effects, enough people are to justify the regulation of it. The most severe effects in both children and adults involve brain and heart damage leading to a coma and eventually death *(5)*.

Cyanide exposure studies have not been able to prove that it directly causes birth defects but there may be an indirect effect. Many people in the tropics eat cassava root and some children are born with thyroid disease as a result of the cyanide and thiocyanate exposure due to their parent's diet *(5)*. People who eat foods containing cyanide over a long period of time have directly been affected by thyroid gland and nervous system problems. Problems with

the thyroid gland result in enlarged thyroids and goiter. Problems with the nervous system cause eye sight problems, deafness, and a lack of muscle coordination. These types of problems are not often seen in the United States because the population's diet does not contain enough cyanide *(11)*. The U.S. EPA has not listed it as a human carcinogen because there are no reports that it causes cancer in humans or animals *(5)*. Regardless of this the health effects that are reported to be caused by cyanide exposure are bad enough to be considered a threat. It is important to determine how to analyze for cyanide accurately, in order to reduce the exposure and threat to those that reside in environments exposed to cyanide from polluted waterways. The United States government has worked to reduce exposure to cyanide and other poisons from polluted waterways beginning with the Clean Water Act *(12)*.

The Clean Water Act

The Federal Water Pollution Control Act of 1948 was expanded and reorganized into the Clean Water Act in 1972. It was written and passed to offer federal protection to the waterways in the United States *(12)*. The water was becoming increasingly polluted and was deemed unsafe for

swimming and fishing. The Act was designed to stop the discharge of pollutants and increase the quality of the water in the environment. The goal of the Clean Water Act was to stop completely the discharge of pollutants and leave the waterways clean enough for swimming and fishing by the year 1985 *(13)*.

The government acknowledges that this is a difficult task to perform both financially and logistically so they offer assistance. The Act provides guidelines and financial assistance to identify and clean up pollution. There are guidelines for facilities that discharge water and financial assistance for the research, construction, and operation of such facilities. State agencies are required to determine the maximum limits of discharge allowed for substances and chemicals and ensure that they are followed *(13)*. However, this is often left up to the U.S. EPA because most states are unable to set the guidelines necessary on their own *(12)*.

Guidelines and Regulations

Anthropogenic cyanide pollution is of great concern and as a result, industries that release it are heavily regulated. The Clean Water Act establishes guidelines for

testing and analyzing cyanide in wastewater because of its toxicity and resulting health effects *(2)*. WWTPs have to follow the regulations set forth by the U.S. EPA under The Clean Water Act in order to receive permits to discharge their treated wastewater.

> Section 301 of the [Clean Water] Act prohibits the discharge of any pollutant into navigable water unless the discharge complies with a [National Pollutant Discharge Elimination System (NPDES)] permit, issued under section 402 of the Act *(2)*.

Cyanide in wastewater has discharge limits set forth by the U.S. EPA depending on the industry and the size of the facility (<38,000 or >38,000 liters per day). In fresh water the U.S. EPA sets the limit at 5.2 ppb total continuous discharge (4 days) and 22 ppb maximum discharges (1 hour). In salt water, continuous and maximum discharge of total cyanide is 1 ppb *(14)*. The NPDES permit limits free cyanide to an 8.5 ppb maximum daily concentration and 4.3 ppb average monthly concentrations *(15)*. If cyanide is found to be above the established limits they are required to report it to the U.S. EPA or their state agency in accordance with the Clean Water Act *(4)*.

Most wastewater treatment plants are receiving permit violations because they are having difficulty complying with these limits. If they do not fix this problem they have the potential of receiving lawsuits from public challengers. The difficulty they have in complying with the limits may be due to interferences from the treatment of the wastewater, as well as, in the required analysis and treatment methods that are available for cyanide *(16)*.

Treatment at Industrial Operations

The industrial operations that are an anthropogenic source of cyanide are regulated. If industrial operations release more cyanide than they are supposed to they are subject to heavy penalties. To avoid heavy penalties they have a variety of methods to pre-treat the cyanide waste before it leaves their plants. The methods most often used are "alkaline chlorination, which converts cyanide to the less toxic cyanate; electrolysis, which converts it to carbon dioxide; or ozonation" *(16)*. After their pretreatment process the wastewater is sent to WWTPs.

The Process of Treatment at Wastewater Treatment Plants

At WWTPs the wastewater is treated according to U.S. EPA regulations and released into the environment. Cyanide analysis at WWTPs repeatedly shows that there are higher levels of cyanide in the effluent after the treatment and disinfection process than there is in the influent before the process *(17)*. Cyanide can still be found in the WWTPs effluent despite their best efforts to treat their wastewater and remove cyanide pollutants. The occurrence of cyanide in the effluent is most likely a result of the treatment and/or analytical processes they use *(16)*. Studies are being done to determine at what point during the treatment or analysis process that cyanide is being generated and how to prevent it from occurring.

Wastewater is treated at treatment plants in four different steps. The influent wastewater goes through preliminary treatment, primary settling basins, secondary treatment, and disinfection to be released as treated effluent. It is important to understand how wastewater is treated to understand what role the treatment process may have in causing interferences.

Preliminary Treatment

The first step is designed to remove all of the large or hard solids that may clog or break other equipment. The equipment used for this process can include "grinders (comminutors), bar screens, and grit channels" *(18)*. The grinders chop up trash, the bar screens catch objects, and the grit channels allow heavy objects to settle out *(18)*.

Primary Settling Basins (Primary Clarifiers)

In the second step the influent water slowly flows for a few hours in a settling tank. This allows the organic suspended matter to settle to the bottom or float to the top. Scrappers at the bottom and skimmers at the top of the basins remove the organic suspended matter once it has settled to the bottom as sludge or floated to the top as scum. The water sans the organic suspended matter moves on to secondary treatment *(18)*.

Secondary Treatment

The third step is biological and is designed to remove all of the remaining dissolved or colloidal organic matter. The biodegradation takes place in a well aerated location suitable for the growth of the microorganisms. The microorganisms commonly seen are mostly bacteria as well as algae, fungi, and protozoa. In this suspended growth

process called an activated sludge system there are two parts. The first part consists of an aeration tank and the second part consists of a settling tank known as a clarifier. The aeration tank promotes microorganism growth by mixing and aerating the water with mechanical aerators located on the surface or compressed air bubblers at the bottom. The growth of sludge occurs as the microorganisms feed on the organic compounds found in the water. The clarifier is where the sludge is collected to be recycled and used over again to treat more water *(18)*.

Disinfection

The last step in the treatment process destroys the pathogenic microorganisms. This process commonly involves the use of chlorine to treat the water and then a dechlorination process involving the addition of other chemicals to remove the chlorine *(19)*. Chlorination/ dechlorination has many problems associated with its use. It has the potential to form chloroform and other halogenated species suspected of being carcinogens with the organic matter. It is known to be toxic to aquatic life found in the receiving waters and it is hazardous to store and handle. Other processes may use ozone or ultraviolet light. Although these processes do not have the many

complications associated with them that chlorine does they tend to be more expensive and so are not readily used *(18)*. The chlorination/dechlorination step in the treatment process is where interferences begin for cyanide analysis.

Testing Methods

Cyanide is known for being "ephemeral" because it has the ability to form and be destroyed in many different ways. As a result testing for cyanide is very problematic *(20)*. The U.S. EPA has acknowledged a discrepancy between the amount of cyanide measured during analysis and the method being used *(21)*. WWTPs use different methods in cyanide analysis depending on the class of cyanide they are testing. Free, available, total, weak acid dissociable, and cyanide amenable to chlorine are tested differently. In some cases the same method may be used to measure the different classes of cyanide.

Available Cyanide

Available, weak acid dissociable, and chlorine amenable to chlorination all are most likely measuring similar groups of species (free, weak, and moderately-bound complexes) with the exact differences unknown. The results

of these methods are the same or very similar to each other because of this.

OIA-1677: Available Cyanide by Flow Injection, Ligand Exchange, and Amperometry. The method detection limit for this method is 0.5 ppb and the minimum reporting level is 2.0 ppb for cyanide analysis. Cyanide is released from weak-to-moderately strong complexes by means of a ligand exchange reagent, and is separated from the sample matrix after neutralization with hydrochloric acid using a hydrophobic gas diffusion membrane. The cyanide is measured amperometrically using a silver electrode with an applied potential of zero volts relative to a silver/silver chloride electrode reference. The time of analysis is about two minutes. This method acknowledges the probability of interferences such as sulfide but offers steps to treat them *(22)*.

Free Cyanide

ASTM D7237-06: Standard Test Method for Aquatic Free Cyanide with Flow Injection Analysis (FIA) Utilizing Gas Diffusion Separation and Amperometric Detection. This method measures the amount of free cyanide in aquatic systems that have a pH of 6-8 at a range of 2 to 500 ppb. It is similar to OIA 1677, which is the method used to

determine available cyanide. The difference is that ligand exchange is not used for the displacement of the cyanide ions and a pH 6-8 buffer is used instead of the hydrochloric acid to employ milder conditions *(23)*. The milder conditions more closely mimic the conditions that would occur when wastewater is discharged into a local body of water. This method still presents the possibility of interferences such as sulfide and care needs to be taken to minimize false cyanide readings.

Total Cyanide

U.S. EPA Method 335.4: Determination of Total Cyanide by Semi-Automated Colorimetry. In this method the cyanide is released from moderately strong to strong complexes as HCN by means of a strong acid reflux-distillation and is absorbed in a scrubber containing a sodium hydroxide solution. The cyanide is analyzed using automated colorimetry with pyridine-barbituric acid chemistry *(24)*. This procedure reduces the time per sample and has less safety concerns than the manual colorimetric methods or macro distillation technique. It is subject to a number of interferences which result in artificially high levels of cyanide being measured *(7)*.

TCN analysis in wastewater samples does not specifically measure each species of cyanide in the wastewater samples. The methods used give a combined measurement of cyanide in the wastewater sampled and do not differentiate between the different cyanide species present. Many different cyanide species reside in wastewater and the identification and quantification of them is not a common practice. This is a problem because as stated earlier, different cyanide species have different toxicity levels and if the species is unknown the toxicity level is unknown. There are limits to using the results from these methods for risk assessment, evaluation of CN^- fate, transportation in the aquatic environment, and the treatment process because TCN does not provide enough specific information *(7)*.

Weak Acid Dissociable Cyanide (WAD)

SM 4500-CN-I: WAD Cyanide by Distillation (Macro Distillation, Colorimetric Finish). The samples are refluxed in a macro cyanide distillation apparatus at a pH of 4.5 in the presence of zinc acetate. The lower acidity doesn't release cyanide from the strong complexes. The distillate is similarly collected in NaOH and analyzed colorimetrically with a pyridine-barbituric acid reagent at

578 nm using a spectrophotometer. The method detection limit is 0.5-2.0 ppb. This method does not have as much interference as CATC and total cyanide. However, interference due to the sample matrix may still create problems *(4, 25)*.

WAD cyanide is identified as cyanide species measured using colorimetric detection techniques. The species identified as WAD cyanide are those that are released at a pH of 4.5. The higher pH allows the cyanide to stay bonded to the strong complexes. WAD species include "HCN (aq) and CN^-, the majority of Cu, Cd, Ni, Zn, Ag complexes and others with similar [...] dissociation constants" *(3)*.

Cyanide Amenable to Chlorine (CATC)

CATC is similar to WAD in that it is identifying weaker complex species that are measured using the same colorimetric detection chemistry. Two measurements are required: a TCN measurement as well as a measurement after chlorination. The chlorination will break down free and available cyanide. The difference that is found between the two measurements is reported *(26)*.

U.S. EPA Method 335.1: Cyanides, Amenable to Chlorination (Titrimetric; Spectrophotometric). Part of the sample is chlorinated at a pH > 11 which breaks down

the CATC. The chlorinated and unchlorinated samples are then analyzed using a total cyanide procedure. The CATC is determined by looking at the difference between the cyanide results in the two different sample types *(27)*. CATC methods may be subject to interferences due to the matrices of the samples.

Modifications of the Current Methods

The Santa Ana Watershed has many wastewater treatment plants that discharge effluent into it. These plants are looking for a uniform method in which to analyze cyanide in their wastewater. The wastewater treatment plants have taken the methods available to them and modified them to ensure compliance with the regulations and keep their permits. The methods used in the laboratories are modified in accordance with the resources that are available. Some plants have modified the method by eliminating the preservation process because they can analyze the samples immediately after collection, and this would circumvent the possible generation of cyanide suspected at high pH. This modification does not work for every facility especially if they have to travel a distance to collect their samples for analysis. Another modification that occurs is the

elimination of distillation before the samples are analyzed. This would allow a measurement of free cyanide. All of the modifications are made to avoid interferences in cyanide analysis.

Interferences

The current methods available for cyanide analysis are susceptible to interferences resulting in false readings. It is hard to prevent this from happening because interfering compounds are potentially produced during the treatment, preservation, distillation, and analysis of wastewater using the approved amperometric and colorimetric methods. Interferences are the biggest reason for the erroneous results that lead to fines for WWTPs. The San Francisco Bay Regional Water Quality Control Board states that "cyanide is a regional problem associated with the analytical protocol for cyanide analysis due to matrix interferences" *(28)*.

Treatment (Chlorination/Dechlorination)

Wastewater goes through a number of treatment processes before it is deemed suitable to release back into the environment. One of the last treatment processes wastewater undergoes at many WWTPs is a chlorination and

dechlorinaton step to kill pathogenic organisms and other contaminants. However, this process contributes to the formation of cyanide. In a study by Weinberg, Cook, and Singer *(16)* it was concluded that water that has been chlorinated results in an increase in cyanide formation possibly through the breakdown of thiocyanate. In chlorinated wastewaters thiocyanate generates free cyanide by undergoing incomplete oxidation. In the same study it was determined that the increased level of cyanide in the effluent after it is completely treated is caused by a fast reaction mechanism associated with the disinfectant and a precursor such as carbon containing organic matter in the wastewater. The contact of chlorine with nitrite in the presence of a carbon precursor appears to increase the cyanide levels at the end of the treatment process and when the sample is preserved and stored at pH 12. They found that WWTPs that used UV lights instead of chlorination to disinfect the effluent did not have problems with cyanide detection. UV lights are very expensive and so many WWTPs can't use them. The best way to deal with the interferences is to make sure all of the residual chlorine and nitrite is removed from the sample when it is collected. Nitrite being removed from the sample

immediately kept the cyanide levels < 5 ppb. This is very important to do in order to get a true reading of the TCN concentration from the sample collected *(16)*.

Preservation

In situ cyanide formation begins at the collection process where samples are preserved in plastic bottles by adjusting the pH $\geq$12 with NaOH or another strong base. While this prevents the loss of volatile hydrogen cyanide by converting it to a non-volatile ionic form it does not prevent cyanide from increasing further *(10)*. Studies have shown that the preservation process found in U.S. EPA method 335.4 can lead to the formation of cyanide in the sample *(20)*. This is a problem for WWTPs that use this method for analyzing cyanide in their wastewater.

A study done by the Los Angeles County Sanitation District determined that the cyanide detected in their effluent was due to the preservation methods they used. While the cyanide levels were below the reporting limit they were still high enough to be detected. In their study they took samples from different treatment plants to see what effect four approved preservation protocols had on TCN analysis *(10)*. Different dechlorinating agents were used and the pH was adjusted to preserve the samples. The

results differed widely but a clear pattern emerged. Immediate analysis without pH adjustment to $\geq$ 12 gave cyanide concentrations below (the) reporting limit of 5 ppb, irrespective of the dechlorinating agents used. When the pH was adjusted to $\geq$ 12, a slight increase in the measured cyanide concentration was observed when thiosulfate was used to dechorinate the samples, and a significant increase (> 10 ppb) was observed when arsenite was used as the dechlorinating agent *(10)*. U.S. EPA method 335.4 recommends these methods yet the results obtained for each sample were different depending on how each was preserved. They determined that performing immediate analysis after dechlorination without adjusting the pH gave the most accurate results. WWTPs are turning to immediate analysis to prevent the artificial formation and loss of cyanide that occurs during storage. Their study shows that adjusting the pH increased the cyanide levels and with immediate analysis the pH does not have to be adjusted and the results are more accurate *(10)*.

This is the practical solution in theory. However not all WWTPs are able to immediately analyze their samples. A study performed at the Massachusetts Water Resource Board also concluded that cyanide can form during conventional

preservation and storage conditions. This study was conducted using treated drinking water instead of wastewater but the same principles were applied. The samples they used were dechlorinated using 10% ascorbic acid, 1% sodium thiosulfate, or 10% sodium thiosulfate. They checked the residual chlorine concentrations and added 10 M NaOH to the samples that needed the pH adjusted to > 12 for preservation. The results showed cyanide absent or close to absent from the samples analyzed immediately and present in the samples that were preserved and stored *(20)*. These results are consistent with results from similar studies that used wastewater. It is apparent that interferences due to the preservation methods are a similar problem in both drinking water and wastewater.

Distillation

A number of significant interferences produce false positive bias during sample analysis when a traditional acid distillation technique is used. These species include: "sulfide, certain oxidizing agents, nitrate or nitrite, thiocyanate, aldehydes, and ketones" *(16)*. In fact, many studies conclude that thiocyanate is created because of the highly acidic conditions used to determine TCN in wastewater during distillation. Csikai and

Barnard *(6)* found that the highly acidic distillation conditions result in thiocyanate converting into cyanide if oxidants are present. Distillation of samples creates additional interferences due to the acidic solution used in its process. Weinberg and Cook *(7)* had the same sample analyzed at three different labs using acid distillation and received different results each time. They concluded that this is because there are a number of interferences and problems with the method. During distillation nitrites will protonate to nitrous acid in the strongly acidic solution. There is a theory that the nitrous acid formed from that process contributes to cyanide formation *(17)*. It was reported in a study performed by Carr that cyanide concentrations went up when nitrite concentrations increased. When using method 4500-CN it is not necessary to remove nitrite until right before the sample is analyzed because this only occurs during distillation *(17)*. Interferences are also produced during distillation at the step that utilizes water cooled condensers to separate the volatile hydrogen cyanide from its acidified matrix. Sebroski and Ode *(4)* believe that the volatile ascorbic acid byproduct is what is causing the interference. There are additional interferences due to the highly acidic

conditions found when distilling. The presence of carbonate in high concentrations has been reported in the 18th edition of Standard Methods for Examination of Water & Wastewater to affect the distillation procedure by causing a violent release of CO_2 leading to excessive foaming when acid is added before distillation. This affects the pH of the absorbing solution and as a result the method suggests the use of $Ca(OH)_2$ instead of NaOH during preservation *(4)*. Interferences caused by the traditional distillation process are thought to be reduced when using the micro-distillation method *(20)*.

Analysis

Interferences that are generated during the course of analysis pose serious difficulties for monitoring and enforcing permits. These interferences present during traditional acid distillation are minimized or absent with the new analytical methods being developed *(16)*. Most standard procedures for cyanide analysis show sulfide interference *(8)*. This interference is the most important to eliminate in order to determine the accurate amount of total cyanide in wastewater. The sulfide reacts in the wastewater and forms hydrogen sulfide which distills with HCN in TCN methods or passes through the gas diffusion

membrane with HCN in amperometric methods. High levels of hydrogen sulfide therefore produce a positive bias by showing up as an apparent cyanide measurement during either of these types of analyses. It is recommended that the samples be treated with lead carbonate to precipitate sulfide and lower the false measurement in the methods that use amperometry *(7)*. Since sulfide and $PbCO_3$ (i.e. PbS) will react with thiocyanate to generate free cyanide by undergoing incomplete oxidation, it is important to remove the PbS precipitate immediately before continuing with the analysis *(8)*.

The U.S. EPA has considered the effects interferences have on the methods and revised 40 CFR Part 136 by adding ways to remove or suppress these "cyanide interferences, including the interferences from sulfur, sulfide, sulfite, thiocyanate, and aldehydes" *(20)*. The analytical methods recognize a number of TCN interferences in the wastewater matrices that provide an inaccurate measurement of cyanide *(16)*. In guidelines set forth by the U.S. EPA, methods to be proposed according to 40 CFR Part 136 should describe any known or potential problem while performing the method and what the source of that problem may be *(2)*. Better methods need to be developed in order to accurately

determine TCN levels in the wastewater. Until then cyanide analysis will continue to be a problem for WWTPs.

Scope of the Project

The environmental impacts from cyanide and the widespread detection of it in the disinfected effluent at WWTPs is a major concern for public utilities and the focus of attention from regulatory entities *(10)*. The conclusion is that that there is not just one source of cyanide generation during the treatment and analysis process. However, finding and fixing the many sources for cyanide generation has proven to be difficult. This results in serious problems for WWTPs. Permit violations received by WWTPs may not be their fault. They are following the testing and analysis guidelines set forth by the U.S. EPA and still are receiving violations for high levels of cyanide that may not be there in the first place. Interferences from the U.S. EPA approved testing and analysis guidelines results in inaccurate cyanide concentration results. This conclusion was made because it is not just one plant that is having problems complying with the levels set. Most WWTPs see the sampling and analytical methods used as a problem and are concerned,

especially since the currently approved methods for determining cyanide have remained unchanged for years despite the problems associated with them *(16)*.

This project examined the interferences that occur while analyzing cyanide in wastewater. The methods used in this project were in accordance with the established methods. The effect NaOH preservation has on cyanide values using both amperometric and colorimetric methods was analyzed. With the amperometric/gas diffusion methods, the effect of using ligand exchange reagents (OIA 1677) was compared to the milder method (ASTM 7237). The effect distillation has on cyanide analysis was studied by running preserved cyanide samples with and without distillation for the colorimetric methods. The effect of removing residual sulfide with $PbCO_3$ on the results was analyzed, and a comparison of results using the macro versus micro distillation is also presented. Analyzing all of these different methods show what works and what doesn't for the wastewater treatment plants in the SARDA region. It is important that uniform methods be developed in order to get readings that are accurate wherever they are tested. This project aimed to do that with the limited time and resources available.

Limitations of the Project

Holding time is an important part of performing accurate cyanide analysis. Cyanide samples must be analyzed within a certain amount of time in order to ensure accurate results. However, with the limited time available this project was unable to address holding time as a factor. With the limited time and equipment available the amount of samples analyzed and the number of WWTPs where the samples were taken prevented the available data from proving statistical significance. More samples need to be analyzed at a number of WWTPs in order to get the statistical significance of the data available. With more time available the samples should be collected throughout the entire year to get a representation of how the water influent chemistry, which changes with the seasons, affects the results.

CHAPTER TWO

METHODOLOGY

Introduction

Wastewater treatment plants (WWTPs) that are part of the Santa Ana Watershed have many different methods for determining cyanide levels in their influent and effluent. The EPA has approved methods for detecting cyanide in wastewater. However, the methods they have approved create problems with inconsistencies and are not feasible for every WWTP to use. Many WWTPs have modified the U.S. EPA approved methods to suit the unique aspects of their facilities needs.

The methods and modifications each WWTP chooses to use depend on a number of factors. These include: where they analyze their samples (on-site or off-site), the equipment available, manpower, and the time available. All of these factors go into customizing a method that will allow WWTPs to produce the best cyanide recovery results while following the guidelines and regulations. The problem is that a method that gives accurate and precise results at one WWTP does not give the same results at another. WWTPs that are members of SARDA are working to develop a uniform

method for detecting cyanide that will give the most accurate and precise results wherever it is performed.

Some issues that need to be addressed in order to determine a uniform method that gives reliable cyanide recovery results include chlorination/dechlorination, sulfide treatment, preservation, distillation, and the type of analysis performed. This project examines the affect preservation and distillation of wastewater samples has on cyanide detection levels using amperometric and colorimetric methods. It also looks at what affect chlorination/dechlorination and sulfide treatment has on cyanide detection. Preserved and non-preserved wastewater samples were analyzed to determine what preservation does to the cyanide levels. Wastewater samples were analyzed using micro distillation and macro distillation to see which yields better cyanide recoveries. Both amperometric and colorimetric methods were used to analyze samples in order to determine the best method for detecting cyanide. All of these issues were examined to aid the members of SARDA in finding a uniform method that gives accurate and precise results at every wastewater treatment plant.

The methods used for macro distillation of effluent and influent wastewater samples were U.S. EPA Method

335.2 *(29)* and Standard Method 4500 *(25)*. LACHAT's QuikChem method 10-204-99-1-X *(30)* was used for micro distillation of effluent wastewater samples. To analyze the wastewater samples colorimetric and amperometric flow injection analysis (FIA) methods were used (LACHAT Quikchem Model 8100, Loveland, Colorado). The colorimetric detection method *(24)* was used to analyze total and free cyanide (no distillation) and the amperometric detection method *(22)* was used to analyze available and free cyanide. Free cyanide was analyzed using both methods by testing non-distilled samples. Total cyanide was analyzed with the colorimetric method using both micro and macro distilled samples. Available cyanide was analyzed using the amperometric method with ligand exchange reagents.

A standard addition method was considered using $C_x=(A_xC_s)/(A_T-A_x)$. With C_x: standard addition concentration, A_x: concentration without the spike, C_s: spike concentration, and A_t: concentration with the spike. Three assumptions needed to be made: the calibration curve is linear, the total volume before and after the spike is more or less equal, and fit concentration values instead of raw peak data were used in the standard addition formula. The standard addition method was considered and determined to

be inappropriate for the data used. The tests are looking for possible real increases and decreases in cyanide and the standard addition method will only correct for other components in the sample matrix that contribute to the cyanide signal. The CN^- loss or gain will be in addition to the matrix interference. Moreover, the samples could not be further diluted as the concentrations observed are too close to the detection limit. With these tests only one standard addition was performed where a few more should be used.

Sample Collection and Preservation

Preparation for Macro Distillation and Colorimetric Analysis

Samples from three WWTPs were collected in 1 liter polyethylene bottles. The bottles were rinsed with de-ionized water and dried before their use. The bottles used for collecting the preserved samples had 15-20 pellets (approximately 2.0-2.5 grams) of NaOH (99%, Fisher Scientific, Fair Lawn, New Jersey) placed in them before collection. Once the samples were taken back to the laboratory at California State University San Bernardino (CSUSB) the pH levels were tested and additional pellets

were added to raise the pH when necessary. The pH for all the samples was measured using a benchtop pH/mV/°C meter (OAKTON, Vernon Hills, Illinois) to ensure accurate measurement. Four samples of influent and four samples of effluent were taken from both the Riverside Water Quality Control Plant (RWQCP) and Inland Empire Utilities Agency (IEUA). Two of the influent samples and two of the effluent samples from each facility were preserved by raising the pH $\geq$ 12. A total of eight samples were collected from each facility. A total of twelve samples were collected from San Bernardino Water Quality Control Plant (SBWQCP): four samples of their Unit 1 secondary effluent, four samples of their Unit 2N secondary effluent, and four samples of their NRC secondary effluent. Two samples of each type collected from SBWQCP were preserved raising the pH $\geq$ 12. The samples were transported from the WWTPs to the laboratory at CSUSB in a cooler and stored in a 4°C temperature monitored refrigerator when not being used. For control sample comparison one 1 L sample of each type collected was spiked with 1mL of 12.61 ppm working CN^- solution resulting in samples that were 12.61 ppb CN^-. The non-preserved samples were analyzed the day they were collected. Of the four non-preserved samples collected

from both the RWQCP and IEUA two samples from each (one effluent and one influent) were macro distilled. Of the six non-preserved samples collected from SBWQCP three were macro distilled (one Unit 1 secondary effluent, one Unit 2N secondary effluent, and one NRC secondary effluent). The remaining ten preserved samples were analyzed within a week of collection. See figure 1.

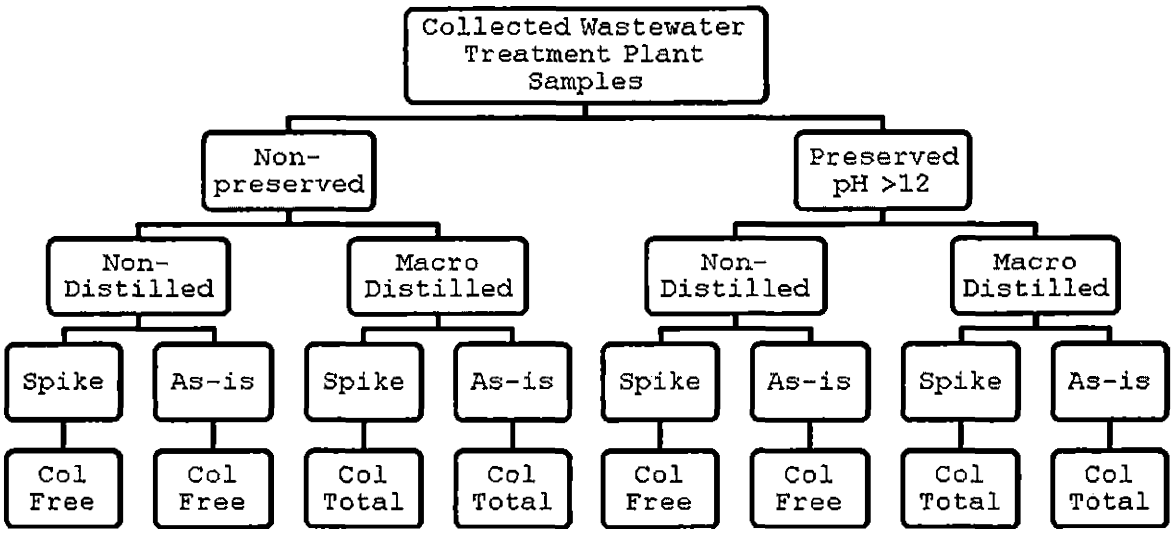

Figure 1. The Treatment Process for Macro Distillation and Colorimetric Analysis. Influent and effluent wastewater samples treated for free and total cyanide detection using colorimetric analysis. Samples were preserved with NaOH pellets. Run 1 spike=12.61 ppb cyanide. As-is=Samples not spiked. Col=Colorimetric analysis.

Preparation for Micro Distillation and Amperometric or Colorimetric Analysis

Wastewater effluent samples from SARDA WWTPs were collected by their facilities and received by the CSUSB laboratory for analysis. The facilities were: IEUA, Yucapia Valley Water District (YVWD), Corona Department of Water and Power (CDWP), RWQCP, and Western Municipal Water District (WMWD). The samples were transported in a cooler and stored in a 4°C temperature monitored refrigerator when not being used. Each WWTP collected and provided two effluent samples. One of those effluent samples was received by the CSUSB laboratory non-preserved and the other sample was preserved by the facilities with NaOH to raise it to pH $\geq$ 11. The pH was measured for all of the samples at CSUSB to ensure they were correct. If the pH was too high the sample was treated with concentrated hydrochloric acid (34-37%, Fisher Scientific, Fair Lawn, New Jersey) to lower the pH to 11 $\pm$ 0.5.

Each sample was split into four-100 mL samples for a total of forty samples in run 2 and five-100 mL samples for a total of fifty samples in run 3. The four-100 mL samples in run 2 and run 3 were: preserved with sulfide treatment, preserved without sulfide treatment, non-preserved with

sulfide treatment, and non-preserved without sulfide treatment. During run 3 the pH was raised to $\geq$ 12 using 1 M NaOH on an additional ten non-preserved samples treated for sulfide. This was to observe how recommended pH levels affect cyanide detection using pH $\geq$ 11 and pH $\geq$ 12. A total of twenty samples were treated for sulfide in run 2 and a total of thirty samples were treated for sulfide in run 3. The samples were treated for sulfide by adding 0.320 g of lead carbonate (100%, Alfa Aesar, Ward Hill, Massachusetts) per 100 mL of sample and filtering out the sulfide precipitate that formed. All of the samples were filtered using a pressure gas filtration apparatus (Millipore, Billerica, Massachusetts). Nitrogen compressed gas (99.998%, Airgas, San Bernardino, California) pushes the sample through acid washed TCLP filters that have a pore size of 0.7 µ and a diameter of 142 mm (Environmental Express, Mt. Pleasant, South Carolina). Sample spikes were performed on the third run to yield added concentrations of 5.5 ppb CN^-. This was done by spiking the 100 mL samples with 550 µL of 5 ppm working CN^- solution. 6 mL of each of the samples were analyzed using amperometric methods for free and available cyanide. See figure 2.

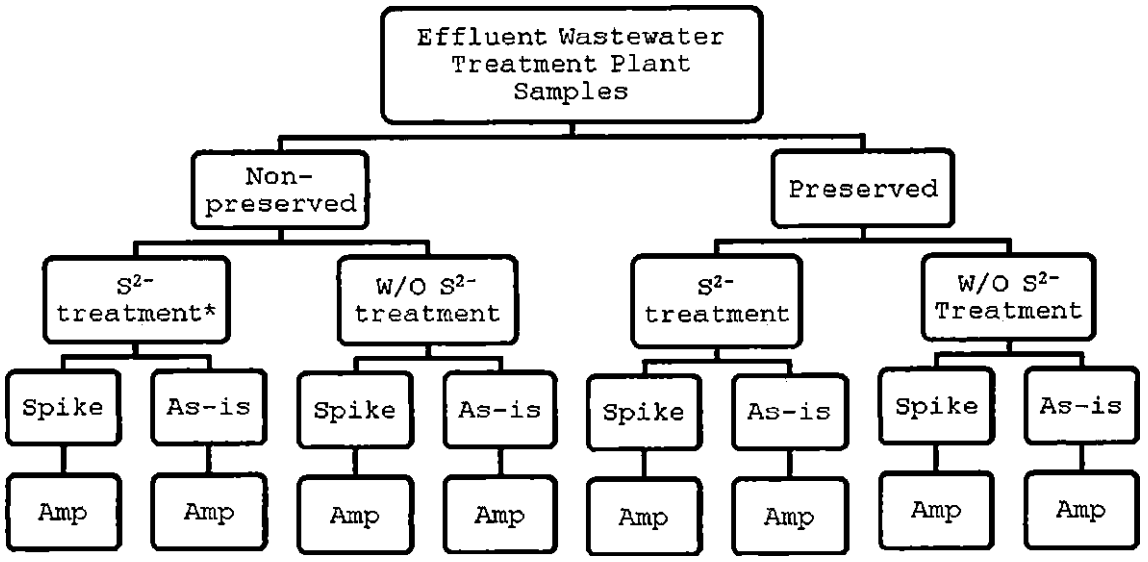

Figure 2. The Treatment Process for Amperometric Analysis. Effluent wastewater samples treated for available and free cyanide detection using amperometric analysis. Samples preserved and the pH was raised with 1 M NaOH. Sulfide was removed from the samples with lead carbonate. Run 2 spike=0.5 ppb cyanide. As-is=Samples not spiked. Run 3 spike=5.5 ppb. Amp=Amperometric analysis for free and available cyanide. *Raised the pH $\geq$12.

6 ml of each sample was micro distilled and the micro distilled samples as well as the non-distilled samples were analyzed using colorimetric methods for free and total cyanide. See figure 3.

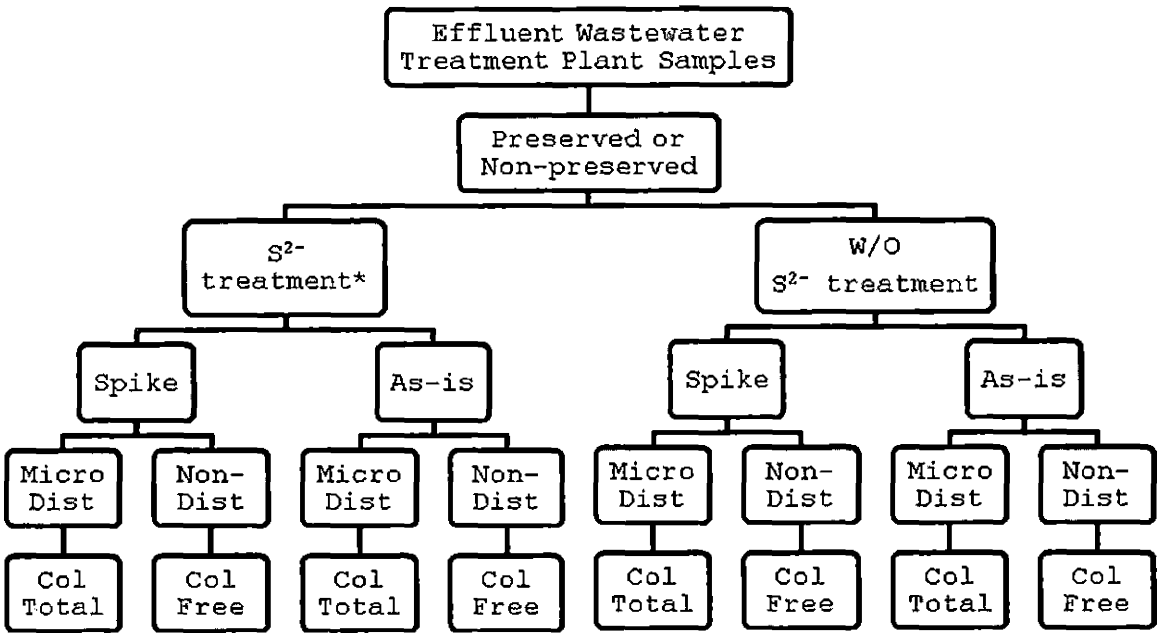

Figure 3. The Treatment Process for Micro Distillation and Colorimetric Analysis. Effluent wastewater samples treated for total and free cyanide detection using colorimetric analysis. Samples preserved and the pH was raised with 1 M NaOH. Sulfide was removed from the samples with lead carbonate. Run 2 spike=0.5 ppb cyanide. Run 3 spike=5.5 ppb. As-is=Samples not spiked. Col=Colorimetric analysis. *Raised the pH $\geq$ 12.

Distillation

Macro Distillation

The samples were macro distilled following EPA approved method 335.2 and Standard Method 4500. The procedure utilized results in the release of cyanide in the

form of HCN from cyanide complexes. The HCN is produced once the sample is acidified and during distillation. The HCN solution is absorbed into the sodium hydroxide containing CN^- receiving scrubber *(25, 29)*.

Setup. A 1 L round-bottom distillation flask was placed on a heater. 50 mL of 0.5 M NaOH solution was added to the CN^- receiving scrubber. 25 mL of 0.079 M lead acetate (99%, Acros Organics, Morris Plains, New Jersey) was added to the sulfide scrubber. The distillation flask, condenser, sulfide scrubber, and CN^- receiving scrubber were all attached. An air flow was started and maintained by adjusting the vacuum source to keep a moderately fast air flow rate (5 air bubbles/second). Cooling water at a temperature of 10°C ran through the condenser throughout the macro distillation procedure. See figure 4.

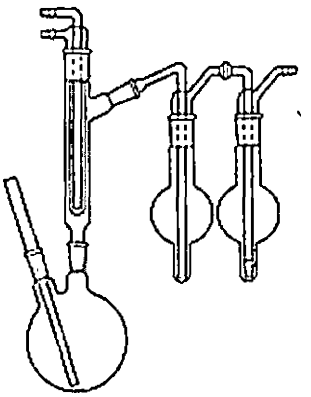

Figure 4. Cyanide Macro Distillation Apparatus. The flasks going left to right are the distilling flask, sulfide scrubber, and cyanide receiving scrubber *(31)*.

Procedure. 500 mL samples were poured into the distilling flask containing 10-12 small glass beads and the air flow was started. 2 g sulfamic acid (99.9%, Fisher Scientific, Fair Lawn, New Jersey), 50 mL 18 M H_2SO_4 solution (95.5%, Fisher Scientific, Fair Lawn, New Jersey), and 20 mL 0.79 M Mg_2Cl_2 solution (99%, ACROS Organics, Morris Plains, New Jersey) were added separately at three minute intervals during reflux to the distilling flask. The inlet tube was washed and rinsed with distilled water after each solution was added. The heat was turned off after one hour of reflux while the air flow continued for fifteen minutes. When the distilling flask was cooled the

absorber was disconnected and the vacuum source was turned off. The solution was drained and washed from the absorber with distilled water into a 100 mL flask. The collected sample was diluted to 100 mL using distilled water and stored in a cool room until analysis. This process was repeated for each sample collected that was intended for macro distillation.

Micro Distillation

The samples were micro distilled using LACHAT QuikChem Method 10-204-00-1-X. The method uses micro distillation to release the cyanide from the sample by digestion and acidification of the cyanide complexes. This converts the cyanide into HCN. The HCN is then absorbed into a diluted 0.25 M NaOH solution *(30)*.

Setup. The micro distillation block was heated to 120°C (LACHAT, MICRO DIST, Loveland, Colorado). The micro distillation tubes were marked at a 6 mL volume from the measurement end. 4 mL of 0.375 M NaOH trap solution was added to the tubes and capped with a membrane. See figure 5.

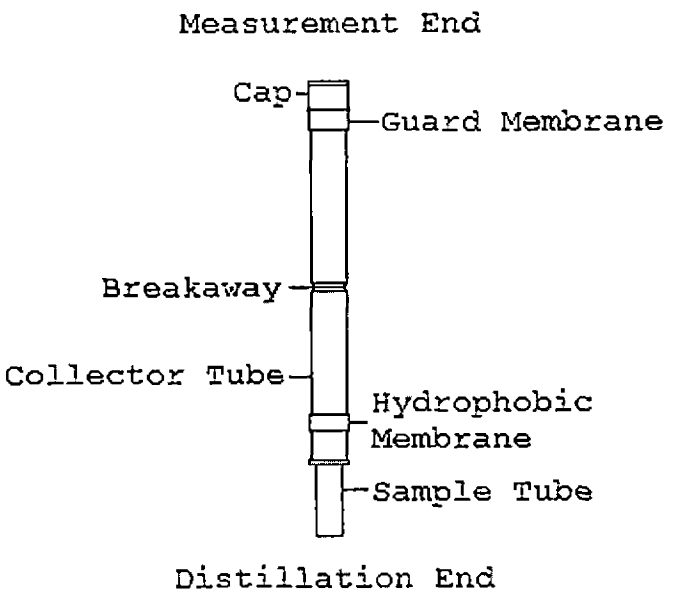

Figure 5. Cyanide Micro Distillation Tube *(32)*.

Procedure. The sample tube was filled with 6mL of sample. 0.75 mL of the 7.11 M H_2SO_4, 0.79 M $MgCl_2$, and 0.33 M H_3NO_3S (sulfamic acid) distillation reagent were added and the sample tube was immediately capped with the distillation tube. The tube was then placed into a vice and sealed by clamping down. The sealed tube was placed into the heating block for 45 minutes. This process was

performed one sample at a time to minimize the loss of cyanide. After 45 minutes, the sample tubes were removed from the heating block and twisted immediately. The measurement end of the tube was opened and deionized water was added to maintain a final volume of 6 mL if necessary. This process was performed on all of the samples requiring micro distillation, including the standards used for calibration. The standards and samples were analyzed immediately after they were micro distilled.

Analysis

Colorimetric Method

The samples were analyzed using flow injection analysis (FIA) with a LACHAT (Quikchem 8500, Loveland, Colorado) using QuikChem Method 10-204-00-1-X. This process of flow injection analysis converts the cyanide into cyanogen chloride (CNCl) by reacting with 0.18 M chloramine T (98%, Sigma-Aldrich, St. Louis, Missouri) at a pH <8. Once this reaction is complete and pyridine-barbituric acid (99%, Spectrum, Gardena, California) is added a red-color complex is formed. The absorbance of the complex is continuously monitored at

570 nm, producing a peak for each injected sample that is directly proportional to the concentration of cyanide *(30)*. Peak areas were determined by the software and a calibration curve was fit to the standard solutions' concentrations. The calibration curve fit was 1^{st} order, 1/X weighting, and calibration by area. The detection limit using this method is 0.5 ppb. The total cyanide in the sample is determined with this method using distilled samples. Free cyanide is determined using this method on samples that have not been distilled.

Procedure. The reagents were degassed with helium (99%, Airgas, San Bernardino, California) for five minutes before they were used. The reagents were pumped through the system to allow for equilibrium for roughly 15 minutes while the unit was heated to 60°C and a stable baseline was obtained. The wash solution for the auto sampler was deionized water. The carrier solution for this method was 0.25 M NaOH and the phosphate buffer solution was 0.71 M KH_2PO_4 (99.6%, Fisher Scientific, Fair Lawn, New Jersey). The samples collected for macro distillation versus non-distillation were analyzed using standard solutions of 0.0, 1.0, 5.0, 10.1, 50.4, and 101.0 ppb CN^- in 0.25 M NaOH. The samples collected for micro

distillation versus non-distillation were analyzed using standard solutions of 0.0, 1.0, 2.0, 5.0, 10.0, 25.0, and 50.0 ppb CN^- in 0.25 M NaOH. The standards and samples were placed onto the autosampler rack, and the instrument timing was programmed according to the parameters specified in the Quikchem method. The system then analyzed the samples and standards made. The peaks were integrated and a calibration curve was prepared for each run to ensure accurate analysis. All of the correlation coefficients were greater than 0.99.

Amperometric Method

U.S. EPA approved method OIA-1677 which is equivalent to LACHAT's QuikChem Method 10-204-00-5-A was used for analysis of available. Free was analyzed by adjusting ASTM 7237 using the same setup described below. This method has two steps to determine available cyanide in a sample: sample pretreatment and cyanide detection. In sample pretreatment ligand exchange reagents are added to the sample. The reagent forms thermodynamic stable complexes with transition metal ions. This results in the release of cyanide from the complexes. The cyanide is then detected using the LACHAT flow injection analysis system. The sample is injected into the flow injection manifold of the

LACHAT. 0.12 M Hydrochloric acid (34-37%, Fisher Scientific, Fair Lawn, New Jersey) is added and converts the cyanide into hydrogen cyanide which then passes under a gas diffusion membrane. The HCN diffuses through the membrane into an alkaline receiving solution (0.025 M NaOH) where it is converted back into a cyanide ion. The cyanide ion is measured amperometrically with an electrode at an applied potential of zero volts versus Ag/AgCl reference electrode. The current that is generated is in direct proportion to the concentration of cyanide present in the sample *(22, 23)*.

Setup. The reagents were degassed with helium for five minutes before they were used. The *petit-ampere* flow cell (BioAnalytical Systems, Inc., MW-5052, West Lafayette, Indiana) consisted of dual silver working electrodes and a separate Ag/AgCl reference electrode. The working electrodes were wiped and polished prior to being used, and the reference electrode was stored in 3 M NaCl when not in use. The potentiostat/ammeter (BioAnalytical Systems, Inc., LC-3D, West Lafayette, Indiana) applied potential was set at 0.00 V, and the background current was offset to 0.00 nA prior to data collection. The reagents were pumped through the system to allow for equilibrium for roughly

15 minutes while the unit was heated to 37°C and a stable baseline was obtained.

Available Cyanide Procedure. The carrier and acceptor solution was 0.025 M NaOH. The standard solutions were 0.0, 1.0, 2.0, 5.0, 10.0, 25.0, and 50.0 ppb CN^- in 0.025 M NaOH. 10 mL of standard and 5 mL of sample were placed in their assigned positions on the autosampler to be analyzed. 100µL 5.3 X 10^{-3} M Ligand Exchange-TEP (tetraethylene-pentamine) solution (Spectrum, Gardena, California) and 500 µL 3.9 X 10^{-4} M Ligand Exchange-Dithizone solution (85%, Spectrum, Gardena, California) was added to each standards tube and swirled to mix. 50 µL Ligand Exchange-TEP solution and 250 µL Ligand Exchange-Dithizone solution was added to each sample tube and swirled to mix. The addition of the ligand exchange reagents was added within two hours of analysis to the samples and standards. This is because the samples and standards are only stable for about two hours after the Ligand Exchange reagents are added. The system then analyzed the samples and standards. The peaks were integrated and a calibration curve was prepared for each run to ensure accurate analysis. The calibration curve was 2^{nd} order, 1/X weighting, and calibration by area. All of the correlation coefficients were greater than 0.99.

Free Cyanide Procedure. The free cyanide detection method also uses a carrier and acceptor solution of 0.025 M NaOH. The standard solutions were 0.0, 1.0, 2.0, 5.0, 10.0, 25.0, and 50.0 ppb CN^- in 0.025 M NaOH. The samples were set to pH 11.0. The pH is set to 11 for analysis of free cyanide because this encourages more complete neutralization with the use of pH 7 phosphate buffer solution instead of strong acid HCl. The standards and samples were placed in the autosampler and the software was programmed precisely like QuikChem method 10-204-00-5-A. The system then analyzed the samples and standards made. The peaks were integrated and a calibration curve was prepared for each run to ensure accurate analysis. The calibration curve was 2^{nd} order, 1/X weighting, and calibration by area. All of the correlation coefficients were greater than 0.99.

CHAPTER THREE

RESULTS

Introduction

The results were analyzed using three methods. One method was to compare different variables within the data sets to determine which yielded higher or lower cyanide results. For example, the preserved samples were compared to the non-preserved samples when reporting preservation results. A second method was to determine how many samples were $\geq$ to 5 ppb CN^- for each variable. The percentage of samples $\geq$ to 5 ppb CN^- was calculated for each variable. 5 ppb CN^- was chosen because it is the reporting limit that is used by WWTPs. A third method was to determine how many samples were non-detectable ($\leq$ 0.5 ppb CN^-) for each variable. The percentage of samples that were non-detectable was calculated for each variable. The non-detectable number was chosen because it is the detection limit for the methods used. In some cases all of the methods were used and in other cases one or two methods were used to analyze the results. The amount of spiked ppb CN^- added was subtracted from the spiked samples and those

samples were included in the results. See table 1 for the detected concentration of the blanks for each run.

Distillation

Influent-Colorimetric-Run 1

The macro distilled influent wastewater samples have a lower amount of total cyanide detected compared to the free cyanide detected in the non-distilled samples. This is true for both the samples spiked with 12.6 ppb CN^- as well as for the samples that were not spiked. The non-distilled method has five free cyanide samples $\geq$ 5 ppb CN^- (63%). The macro distilled method has zero total cyanide samples $\geq$ 5 ppb CN^- (See table 2).

Effluent-Colorimetric-Run 1

The macro distilled effluent wastewater samples have a lower amount of total cyanide detected compared to the free cyanide detected in the non-distilled samples, with the exception of the RWQCP non-preserved sample. All of the macro distilled samples spiked with 12.6 ppb CN^- are lower than the non-distilled spiked samples. The non-distilled method has eight free cyanide samples $\geq$ 5 ppb CN^- (40%). The macro distilled method has two total cyanide samples $\geq$ 5 ppb CN^- (10%) (See table 3).

Effluent-Colorimetric-Run 2

The micro distilled effluent wastewater samples are higher in all of IEUA's preserved total cyanide samples, as well as, RWQCP's preserved without treatment for sulfide spiked sample. The non-preserved micro distilled effluent wastewater samples are higher in all of IEUA and CDWP's total cyanide samples, as well as, all of RWQCP's samples with the exception of the sulfide treated spike sample. The non-distilled method has six free cyanide samples $\geq$ 5 ppb CN^- (15%) while the micro distilled method has three total cyanide samples $\geq$ 5 ppb CN^- (8%). The micro distilled method has four total samples that are non-detectable (10%) and the non-distilled method has three free samples that are non-detectable (8%) (See tables 6 and 7).

Effluent-Colorimetric-Run 3

The micro distilled effluent wastewater samples have a lower amount of total cyanide detected compared to the free cyanide detected in the non-distilled samples, with one exception. The IEUA spiked sample that is non-preserved and not treated for sulfide is higher in the micro distilled method. There are twenty-nine non-detectable total cyanide samples (58%) in the micro distilled method.

There are four non-detectable free cyanide samples (8%) in the non-distilled method. The non-distilled method has twenty-two free cyanide samples $\geq$ 5 ppb CN^- (44%) while the micro distilled method has zero total samples $\geq$ 5 ppb CN^- (See tables 8 and 9).

Sodium Hydroxide Preservation

Influent-Colorimetric-Run 1

The spiked preserved influent wastewater samples have a higher amount of free and total cyanide detected compared to the spiked non-preserved samples. The preserved influent wastewater spiked samples have a lower amount of free and total cyanide detected compared to the non-preserved samples with the exception of the non-distilled sample from RWQCP. The preserved samples have two free cyanide samples that are $\geq$ 5 ppb CN^- (50%) while the non-preserved samples have three that are $\geq$ 5 ppb (75%). None of the preserved or non-preserved total cyanide samples are $\geq$ 5 ppb CN^-. There are three preserved total cyanide samples that are non-detectable (75%) and two non-preserved total cyanide samples that are non-detectable (50%). None of the preserved or non-preserved free cyanide samples are non-detectable (See table 2).

Effluent-Colorimetric-Run 1

The preserved effluent wastewater samples have higher free and total cyanide detected in both distilled and non-distilled samples compared to the non-preserved samples. The preserved samples have eight free cyanide samples (80%) and two total cyanide samples $\geq$ 5 ppb CN^- (20%) while the non-preserved samples have zero free and total cyanide samples $\geq$ 5 ppb CN^-. The preserved samples have one total cyanide sample that is non-detectable (10%) and the non-preserved samples have eight non-detectable total cyanide samples (80%). There are zero preserved and zero non-preserved free cyanide samples that are non-detectable (See table 3).

Effluent-Free Amperometric-Run 2

The effluent wastewater samples have higher amounts of free cyanide in the preserved samples compared to the non-preserved samples with the exception of WMWD's sample treated for sulfide and YVWD's spiked sample that was treated for sulfide. The preserved samples have nine free cyanide samples $\geq$ 5 ppb CN^- (45%) while the non-preserved samples have four free cyanide samples $\geq$ 5 ppb CN^- (20%). There are zero preserved and zero non-preserved free cyanide samples that are non-detectable (See table 4).

Effluent-Available Amperometric-Run 2

The effluent wastewater samples have higher amounts of available cyanide detected in the preserved samples compared to the non-preserved samples with the exception of the spiked samples treated for sulfide from YVWD, CDWP, and WMWD. None of the preserved or non-preserved samples are $\geq$ 5 ppb CN^-. There are sixteen non-preserved (80%) and eight preserved available cyanide samples (40%) that are non-detectable (See table 5).

Effluent-Free Colorimetric-Run 2

The effluent samples has higher free cyanide amounts in the preserved method compared to the non-preserved method with the exception of both the spike and non-spiked samples from YVWD that were treated for sulfide. The preserved method has six free cyanide samples $\geq$ 5 ppb CN^- (30%) and the non-preserved method has zero free cyanide samples $\geq$ 5 ppb CN^-. There are three non-preserved (15%) and zero preserved free cyanide samples that are non-detectable (See table 6).

Effluent-Total Colorimetric-Run 2

The effluent wastewater samples have higher total cyanide amounts in the preserved samples compared to the non-preserved samples with some exceptions. The non-

preserved amounts are higher in the samples treated for sulfide from WMWD, IEUA, and YVWD. The non-preserved amounts are higher in the YVWD spike sample treated for sulfide. The non-preserved amounts are higher in the IEUA and WMWD spiked samples not treated for sulfide. The preserved method has two total cyanide samples $\geq$ 5 ppb CN^- (10%) and the non-preserved method has one total cyanide sample $\geq$ 5 ppb CN^- (5%). One preserved sample (5%) and three non-preserved samples (15%) are non-detectable (See table 7).

Effluent-Free Colorimetric-Run 3

The effluent wastewater samples have higher free cyanide amounts in the preserved samples compared to the non-preserved samples with the exception of the IEUA, YVWD, and WMWD non-preserved samples treated for sulfide. There are eleven non-preserved samples that are $\geq$ 5 ppb CN^- (37%) and eleven preserved samples that are $\geq$ 5 ppb CN^- (55%). One preserved sample (5%) and three non-preserved samples (10%) are non-detectable (See table 8).

Effluent-Total Colorimetric-Run 3

The effluent wastewater samples have higher amounts of total cyanide in the preserved samples compared to the non-preserved samples with a few exceptions. Both the spiked

and non-spiked IEUA and YVWD non-preserved samples treated for sulfide and the spiked IEUA non-preserved sample that was not treated for sulfide are higher. There are zero preserved and zero non-preserved total cyanide samples $\geq$ 5 ppb CN^-. Nineteen non-preserved samples (63%) are non-detectable and ten preserved samples (50%) are non-detectable (See table 9).

Chlorination and Dechlorination

Influent-Colorimetric-Run 1

The total cyanide samples that were chlorinated and dechlorinated are higher in the preserved and non-preserved samples compared to the total cyanide samples that were not chlorinated and dechlorinated. The free cyanide samples that were chlorinated and dechlorinated are lower in the preserved and non-preserved samples compared to the free cyanide samples that were not chlorinated and dechlorinated. One free cyanide sample (25%) and zero total cyanide samples that were chlorinated and dechlorinated are $\geq$ 5 ppb CN^-. Two total cyanide samples (50%) and zero free cyanide samples that were chlorinated and dechlorinated are non-detectable. Four free cyanide samples (100%) and zero total cyanide samples that were not

chlorinated and dechlorinated are $\geq$ 5 ppb CN^-. Three total cyanide samples (75%) and zero free cyanide samples that were not chlorinated and dechlorinated are non-detectable (See table 2).

Effluent-Colorimetric-Run 1

The non-preserved samples that were chlorinated and dechlorinated have similar free cyanide and total cyanide amounts. The preserved samples that were chlorinated and dechlorinated have higher free and total cyanide amounts compared to the samples that were not chlorinated and dechlorinated. Two free cyanide samples (50%) and one total cyanide sample (25%) that were chlorinated and dechlorinated are $\geq$ 5 ppb CN^-. One total cyanide sample (25%) and zero free cyanide samples that were chlorinated and dechlorinated are non-detectable. Six free cyanide samples (38%) and one total cyanide sample (6%) that were not chlorinated and dechlorinated are $\geq$ 5 ppb CN^-. Eight total cyanide samples (50%) and zero free cyanide samples that were not chlorinated and dechlorinated are non-detectable (See table 3).

Effluent-Free Amperometric-Run 2

The non-preserved samples that were chlorinated and dechlorinated are lower than the non-preserved samples that

were not. The non-preserved chlorinated and dechlorinated method has zero free cyanide samples $\geq$ 5 ppb CN^- while the non-preserved samples that were not chlorinated and dechlorinated have four free cyanide samples $\geq$ 5 ppb CN^- (33%). The preserved chlorinated and dechlorinated samples are higher than the preserved samples that were not. The preserved chlorinated and dechlorinated method has five free cyanide samples $\geq$ 5 ppb CN^- (63%) and the preserved samples that were not chlorinated and dechlorinated have four free cyanide samples $\geq$ 5 ppb CN^- (33%). There are zero non-detectable free cyanide samples in this run (See table 4).

Effluent-Available Amperometric-Run 2

The non-preserved samples that were chlorinated and dechlorinated have lower amounts of available cyanide compared to the non-preserved samples that were not. None of the non-preserved samples have available cyanide levels $\geq$ 5 ppb CN^-. None of the preserved samples have available cyanide $\geq$ 5 ppb CN^-. Eight of the non-preserved samples (100%) and one preserved sample that were chlorinated and dechlorinated (13%) have non-detectable available cyanide. Eight of the non-preserved samples (67%) and seven

preserved samples (58%) that were not chlorinated and dechlorinated are non-detectable (See table 5).

Effluent-Free Colorimetric-Run 2

The non-preserved samples that were chlorinated and dechlorinated have a lower amount of free cyanide compared to the non-preserved samples that were not. None of the non-preserved samples have free cyanide detections $\geq$ 5 ppb CN^-. The preserved chlorinated and dechlorinated method has four free cyanide samples $\geq$ 5 ppb CN^- (50%) while the preserved samples that were not chlorinated and dechlorinated have two free cyanide samples $\geq$ 5 ppb CN^- (17%). One chlorinated and dechlorinated non-preserved sample is non-detectable for cyanide (13%) (See table 6).

Effluent-Total Colorimetric-Run 2

The non-preserved samples that were chlorinated and dechlorinated are similar to the samples that were not. There is one non-preserved sample that was chlorinated and dechlorinated that has total cyanide $\geq$ 5 ppb CN^- (13%). There are zero non-preserved samples that were not chlorinated and dechlorinated that have total cyanide $\geq$ 5 ppb CN^-. Both the preserved samples that were chlorinated and dechlorinated (13%) and the preserved samples that were not (8%) have one total cyanide sample $\geq$ 5 ppb CN^-. Three

non-preserved samples (25%) and one preserved sample (8%) that were not chlorinated and dechlorinated have total cyanide samples that are non-detectable (See table 7).

Effluent-Free Colorimetric-Run 3

There are three chlorinated and dechlorinated samples that are non-detectable (15%). There is one free cyanide sample that was not chlorinated and dechlorinated that is non-detectable (3%). Seven of the chlorinated and dechlorinated samples (35%) and fifteen of free cyanide samples (50%) that are not chlorinated and dechlorinated are $\geq$ 5 ppb CN^- (See table 8).

Effluent-Total Colorimetric-Run 3

There are two chlorinated and dechlorinated preserved samples that are non-detectable (17%). Eight of the preserved samples that are not chlorinated and dechlorinated are non-detectable (44%). In the non-preserved method six of the samples that are chlorinated and dechlorinated (75%) and thirteen of the samples that are not chlorinated and dechlorinated (39%) are non-detectable. Zero total cyanide samples are $\geq$ 5 ppb CN^- (See table 9).

Sulfide Treatment

Effluent-Free Amperometric-Run 2

The non-preserved samples from YVWD, CDWP, and RWQCP have higher cyanide detections when the samples were treated for sulfide compared to no treatment. IEUA and WMWD have higher free cyanide amounts in the non-preserved samples that were not treated for sulfide. In the preserved samples IEUA and YVWD has higher cyanide amounts with the samples treated for sulfide compared to the samples without sulfide treatment. CDWP, RWQCP, and WMWD have higher free cyanide amounts in the preserved samples that were not treated for sulfide compared to the preserved samples treated for sulfide (See table 4).

Effluent-Available Amperometric-Run 2

The non-preserved samples from YVWD, CDWP, and RWQCP have higher cyanide amounts when the samples were treated for sulfide compared to the samples without treatment. In the preserved samples IEUA, CDWP, and RWQCP have higher cyanide amounts with the treatment of sulfide compared to samples without treatment. WMWD has higher amounts of cyanide in the preserved sample that was not treated for sulfide compared to the WMWD sample treated for sulfide (See table 5).

Effluent-Free Colorimetric-Run 2

The non-preserved samples from YVWD, CDWP, and RWQCP have higher amounts of free cyanide with the treatment of sulfide compared to no treatment. IEUA and WMWD have higher amounts of free cyanide in the non-preserved samples that were not treated for sulfide. In the preserved samples IEUA, CDWP, and RWQCP have higher amounts of free cyanide with the treatment of sulfide compared to no treatment. WMWD and YVWD have higher free cyanide amounts in the preserved samples that were not treated for sulfide (See table 6).

Effluent-Total Colorimetric-Run 2

The non-preserved samples from all of the WWTPs have higher amounts of total cyanide with the treatment for sulfide compared to no treatment. In the preserved samples IEUA, YVWD, CDWP, and RWQCP have higher amounts of total cyanide detected with the treatment for sulfide compared to no treatment. WMWD has higher amounts of total cyanide detected in the preserved samples that were not treated for sulfide compared to the WMWD samples treated for sulfide (See table 7).

Effluent-Free Colorimetric-Run 3

Non-preserved samples that were treated with sulfide have higher amounts of free cyanide detected compared to samples that were not treated with sulfide. Preserved samples that were treated for sulfide from IEUA, CDWP, and RWQCP are higher compared to the preserved samples not treated for sulfide (See table 8).

Effluent-Total Colorimetric-Run 3

Non-preserved samples that were treated with sulfide have higher amounts of cyanide detected compared to samples that were not treated with sulfide. Preserved samples that were treated for sulfide from IEUA, CDWP, and RWQCP are higher than the samples not treated for sulfide (See table 9).

pH

Effluent-Free Colorimetric-Run 3

The non-preserved samples that were preserved to pH $\geq$12 and treated for sulfide have a higher amount of free cyanide compared to the samples that were preserved upon collection to pH $\geq$11 with the exception of CDWP's sample that was treated for sulfide (See table 8).

Effluent-Total Colorimetric-Run 3

The non-preserved samples that were treated for sulfide and preserved to pH $\geq$12 have a lower amount of total cyanide detected compared to the samples that were preserved upon collection to pH $\geq$11 with some exceptions. YVWD's samples that were pH $\geq$12 and WMWD and IEUA's spiked samples that were pH $\geq$12 are higher than the samples that were pH $\geq$11 (See table 9).

Macro Distillation versus Micro Distillation

Macro distillation has fourteen out of twenty-eight cyanide samples that are non-detectable (50%) (See tables 2 and 3). Micro distillation has four out of forty cyanide samples that are non-detectable in run 2 (10%) (See table 7). Micro distillation has twenty-nine out of fifty cyanide samples that are non-detectable in run 3 (58%) (See table 9). One micro distilled total cyanide sample is above 5 ppb CN^- detection at 7.62 ppb in run 2. However, in run 3 the sample went down to 1.99 ppb. No macro distilled samples are above 5 ppb CN^- detection.

Influent versus Effluent

IEUA and RWQCP provided a total of sixteen influent samples which are compared to the sixteen effluent samples they provided. Influent has five samples that are detected $\geq$ 5 ppb CN^- (31%). Two of those samples were preserved (25%) and three were non-preserved samples (38%). Influent has five samples that are non-detectable (31%). Three of those samples were preserved (38%) and two were non-preserved samples (25%) (See table 2). Effluent has ten samples that are detected $\geq$ 5 ppb CN^- (63%). All ten were preserved samples. Effluent has nine samples that are non-detectable (56%). One was preserved (13%) and eight were non-preserved samples (100%) (See table 3).

Table 1. Detected Concentrations of Blanks

Influent-Colorimetric-Run 1	
Non-preserved IEUA	0.2 ppb
Non-preserved RWQCP	0.1 ppb
Preserved IEUA	0.1 ppb
Preserved RWQCP	0.3 ppb
Effluent-Colorimetric-Run 1	
Non-preserved IEUA	0.1 ppb
Non-preserved RWQCP	0.1 ppb
Non-preserved SBWD Unit 1, Unit 2N, and Unit NRC	0.2 ppb
Preserved IEUA	0.1 ppb
Preserved RWQCP	0.1 ppb
Preserved SBWD Unit-1	-0.2 ppb
Preserved SBWD Unit-2N	1.0 ppb
Preserved SBWD NRC	1.0 ppb
Effluent-Free Amperometric-Run 2	
Non-preserved/Preserved	0.4 ppb
Effluent-Available Amperometric-Run 2	
Non-preserved/Preserved	-0.5 ppb
Effluent-Free Colorimetric-Run 2	
Non-preserved/Preserved	1.0 ppb
Effluent-Total Colorimetric-Run 2	
Non-preserved/Preserved	0.2 ppb
Effluent-Free Colorimetric-Run 3	
Non-preserved/Preserved	0.6 ppb
Effluent-Total Colorimetric-Run 3	
Non-preserved/Preserved	0.2 ppb

The detected concentrations of the blank for each run in ppb CN^-.

Table 2. Influent-Colorimetric-Run 1

Influent					
Colorimetric		Direct	Distilled	Direct, Spiked	Distilled, Spiked
Non-Preserved					
IEUA	ppb CN^-	11.4	1.9	15.1	10
	H.T.	12h 11m	8h	12h 12m	8h
RWQCP	ppb CN^-	12.4	0.8	18	6.6
	H.T.	8h 50m	1h 30m	8h 52m	3h
Preserved					
IEUA	ppb CN^-	4	0.8	16.3	11.3
	H.T.	177h 23m	174h	177h 24m	174h
RWQCP	ppb CN^-	29.1	N.D.	32.3	10.2
	H.T.	53h 9m	49h	53h 10m	51h 30m

Run 1. Amount of cyanide (ppb) detected in preserved and non-preserved influent wastewater samples that were macro distilled for total cyanide detection and not distilled for free cyanide detection and analyzed using colorimetric methods. Shaded samples were chlorinated and dechlorinated before collection. H.T.=Holding Time. N.D.=Non-detectable ($\leq$ 0.5 ppb CN^-). Samples were preserved to pH $\geq$ 12 with NaOH pellets. Spiked=12.61 ppb CN^-.

Table 3. Effluent-Colorimetric-Run 1

Effluent					
Colorimetric		Direct	Distilled	Direct, Spiked	Distilled, Spiked
Non-Preserved					
IEUA	ppb CN^-	2.9	1.7	13.9	4.2
	H.T.	80h 24m	76h	80h 26m	76h
RWQCP	ppb CN^-	2.2	2.8	14.2	10.2
	H.T.	8h 54m	4h 30m	8h 55m	6h
SBWD UNIT-1	ppb CN^-	2.7	N.D.	16.2	9.8
	H.T.	7h 16m	1h 48m	7h 18m	1h 48m
SBWD UNIT-2N	ppb CN^-	1.1	N.D.	16.2	10.8
	H.T.	7h 11m	3h 10m	7h 13m	3h 10m
SBWD NRC	ppb CN^-	1.2	N.D.	16.8	6
	H.T.	7h 5m	5h 30m	7h 6m	5h 30m
Preserved					
IEUA	ppb CN^-	12.4	9.6	27	13.4
	H.T	222h 3m	220h	222h 5m	220h
RWQCP	ppb CN^-	8.9	6.4	21.3	15.8
	H.T	172h 45m	168h	172h 45m	168h
SBWD UNIT-1	ppb CN^-	3.3	1.3	18.2	15.4
	H.T	51h 1m	48h 18m	51h 2m	48h 18m
SBWD UNIT-2N	ppb CN^-	2.7	1.4	19.4	12.9
	H.T	72h 10m	71h 50m	72h 20m	71h 50m
SBWD NRC	ppb CN^-	5	1.4	25.2	15.2
	H.T	169h 11m	167h 30m	169h 13m	167h 30m

Run 1. Amount of cyanide (ppb) detected in preserved and non-preserved effluent wastewater samples that were macro distilled for total cyanide detection and not distilled for free cyanide detection and analyzed using colorimetric methods. Shaded samples were chlorinated and dechlorinated before collection. H.T.=Holding Time. N.D.=Non-detectable ($\leq$ 0.5 ppb CN^-). Samples were preserved to pH $\geq$ 12 with NaOH pellets. Spiked=12.61 ppb CN^-.

Table 4. Effluent-Free Amperometric-Run 2

Free Cyanide Amperometric		S^{2-} trtment	S^{2-} trtment, Spike	W/O S^{2-} trtment	W/O S^{2-} trtment, Spike
Non-Preserved					
IEUA	ppb CN^-	1.1	1.6	3.6	3.7
	H.T.	12h 10m	12h 13m	12h 17m	12h 21m
YVWD	ppb CN^-	6.1	5.5	2.8	4
	H.T.	N/A	N/A	N/A	N/A
CDWP	ppb CN^-	4.5	4.6	4.3	4.3
	H.T.	12h 56m	13h	13h 3m	13h 7m
RWQCP	ppb CN^-	5.1	5.5	4.4	4.5
	H.T.	13h 9m	13h 13m	13h 17m	13h 21m
WMWD	ppb CN^-	2.7	3.3	2.8	2.9
	H.T.	18h 29m	18h 33m	18h 37m	18h 40m
Preserved					
IEUA	ppb CN^-	5.1	5.4	4.7	5.1
	H.T.	12h 28m	12h 32m	12h 36m	12h 40m
YVWD	ppb CN^-	3.5	3.4	3.2	2.7
	H.T.	N/A	N/A	N/A	N/A
CDWP	ppb CN^-	5.9	7.6	7.3	7.8
	H.T.	13h 11m	13h 15m	13h 19m	13h 23m
RWQCP	ppb CN^-	6.2	6.4	6.5	6
	H.T.	13h 25m	13h 29m	13h 33m	13h 37m
WMWD	ppb CN^-	0.7	3.4	3.3	3.9
	H.T.	18h 44m	18h 48m	18h 52m	18h 56m

Run 2. Amount of cyanide (ppb) detected in preserved and non-preserved effluent wastewater samples for free cyanide detection which was analyzed using amperometric methods. Shaded samples were chlorinated and dechlorinated before collection. H.T.=Holding Time. N/A=Not Available. Samples were preserved to pH $\geq$ 11 with 1 M NaOH. Lead Carbonate was added to samples treated for sulfide. Spiked=0.5 ppb CN^-.

Table 5. Effluent-Available Amperometric-Run 2

Available Cyanide Amperometric		S^{2-} trtment	S^{2-} trtment, Spike	W/O S^{2-} trtment	W/O S^{2-} trtment, Spike
Non-Preserved					
IEUA	ppb CN^-	N.D.	0.5	N.D.	N.D.
	H.T.	15h 37m	15h 41m	15h 45m	15h 49m
YVWD	ppb CN^-	0.9	1.6	N.D.	N.D.
	H.T.	N/A	N/A	N/A	N/A
CDWP	ppb CN^-	0.5	0.9	N.D.	0.7
	H.T.	16h 23m	16h 27m	16h 31m	16h 35m
RWQCP	ppb CN^-	1.2	2	N.D.	N.D.
	H.T.	16h 37m	16h 41m	16h 45m	16h 48m
WMWD	ppb CN^-	N.D.	1	N.D.	N.D.
	H.T.	21h 56m	22h	22h 4m	22h 8m
Preserved					
IEUA	ppb CN^-	2.5	3.8	1.8	2.5
	H.T.	15h 56m	16h	16h 4m	16h 8m
YVWD	ppb CN^-	N.D.	0.7	N.D.	0.7
	H.T.	N/A	N/A	N/A	N/A
CDWP	ppb CN^-	3.5	N.D.	2.2	4.9
	H.T.	16h 39m	16h 43m	16h 47m	16h 51m
RWQCP	ppb CN^-	3.4	4.5	1.7	2.5
	H.T.	16h 52m	16h 56m	17h	17h 4m
WMWD	ppb CN^-	N.D.	N.D.	2.7	N.D.
	H.T.	22h 12m	22h 16m	22h 20m	22h 23m

Run 2. Amount of cyanide (ppb) detected in preserved and non-preserved effluent wastewater samples using ligand exchange for available cyanide detection and analyzed using amperometric methods. Shaded samples were chlorinated and dechlorinated before collection. H.T.=Holding Time. N/A=Not Available. N.D.=Non-detectable ($\leq$ 0.5 ppb CN^-). Samples were preserved to pH $\geq$ 11 with 1 M NaOH. Lead Carbonate was added to samples treated for sulfide. Spiked=0.5 ppb CN^-.

Table 6. Effluent-Free Colorimetric-Run 2

Free Cyanide Colorimetric		S^{2-} trtment	S^{2-} trtment, Spike	W/O S^{2-} trtment	W/O S^{2-} trtment, Spike
Non-Preserved					
IEUA	ppb CN^-	N.D.	0.6	0.6	0.9
	H.T.	19h 41m	19h 41m	19h 42m	19h 43m
YVWD	ppb CN^-	4.1	3.8	1.5	1.9
	H.T.	N/A	N/A	N/A	N/A
CDWP	ppb CN^-	2.4	2.8	1.8	2.2
	H.T.	19h 37m	19h 38m	19h 39m	19h 40m
RWQCP	ppb CN^-	2.6	2.9	1.7	1.9
	H.T.	19h 26m	19h 27m	19h 28m	19h 29m
WMWD	ppb CN^-	2.2	2.4	2.2	2.4
	H.T.	24h 21m	24h 22m	24h 23m	24h 24m
Preserved					
IEUA	ppb CN^-	2.5	3.4	1.8	2.1
	H.T.	19h 47m	19h 48m	19h 49m	19h 50m
YVWD	ppb CN^-	1.5	2.1	2.4	2.5
	H.T.	N/A	N/A	N/A	N/A
CDWP	ppb CN^-	5.9	6.6	5.6	6.6
	H.T.	19h 41m	19h 42m	19h 42m	19h 43m
RWQCP	ppb CN^-	6.2	6.7	4.9	5
	H.T.	19h 30m	19h 30m	19h 31m	19h 32m
WMWD	ppb CN^-	2.4	2.9	2.5	3
	H.T.	24h 24m	24h 25m	24h 26m	24h 27m

Run 2. Amount of cyanide (ppb) detected in preserved and non-preserved effluent wastewater samples for free cyanide detection which was analyzed using colorimetric methods. Shaded samples were chlorinated and dechlorinated before collection. H.T.=Holding Time. N/A=Not Available. N.D.=Non-detectable ($\leq$ 0.5 ppb CN^-). Samples were preserved to pH $\geq$ 11 with 1 M NaOH. Lead Carbonate was added to samples treated for sulfide. Spiked=0.5 ppb CN^-.

Table 7. Effluent-Total Colorimetric-Run 2

Total Cyanide Colorimetric		S^{2-} trtment	S^{2-} trtment, Spike	W/O S^{2-} trtment	W/O S^{2-} trtment, Spike
Non-Preserved					
IEUA	ppb CN^-	7.6	1.3	2.1	3.3
	H.T.	20h 33m	20h 34m	20h 35m	20h 35m
YVWD	ppb CN^-	3	3	0.6	0.7
	H.T.	N/A	N/A	N/A	N/A
CDWP	ppb CN^-	2.7	3.3	2.7	2.7
	H.T.	20h 29m	20h 30m	20h 31m	20h 32m
RWQCP	ppb CN^-	2.8	2.6	2.4	2.2
	H.T.	20h 18m	20h 19m	20h 20m	20h 21m
WMWD	ppb CN^-	0.6	0.8	N.D.	1.4
	H.T.	25h 13m	25h 14m	25h 15m	25h 16m
Preserved					
IEUA	ppb CN^-	4.9	5.4	3.7	3
	H.T.	20h 39m	20h 40m	20h 41m	20h 42m
YVWD	ppb CN^-	1	1.9	0.6	1.1
	H.T.	N/A	N/A	N/A	N/A
CDWP	ppb CN^-	5	4.8	4.1	4.9
	H.T.	20h 33m	20h 34m	20h 35m	20h 36m
RWQCP	ppb CN^-	4.9	6.5	4.2	5.4
	H.T.	20h 22m	20h 23m	20h 23m	20h 24m
WMWD	ppb CN^-	0.4	1.1	0.6	1.2
	H.T.	25h 17m	25h 18m	25h 18m	25h 19m

Run 2. Amount of cyanide (ppb) detected in preserved and non-preserved effluent wastewater samples that were micro distilled for total cyanide detection and analyzed using colorimetric methods. Shaded samples were chlorinated and dechlorinated before collection. H.T.=Holding Time. N/A=Not Available. N.D.=Non-detectable ($\leq$ 0.5 ppb CN^-). Samples were preserved to pH $\geq$ 11 with 1 M NaOH. Lead Carbonate was added to samples treated for sulfide. Spiked=0.5 ppb CN^-.

Table 8. Effluent-Free Colorimetric-Run 3

Free Cyanide Colorimetric		S^{2-} trtment	S^{2-} trtment, Spike	W/O S^{2-} trtment	W/O S^{2-} trtment, Spike	S^{2-} trtment, pH≥12	S^{2-} trtment, Spike pH≥12
Non-Preserved							
IEUA	ppb CN^-	2.7	10	0.6	3.9	2.5	10
	H.T.	57h 30m	57h 31m	56h 58m	56h 59m	56h 56m	56h 57m
YVWD	ppb CN^-	7.3	10	2.5	8.8	6.7	13.1
	H.T.	N/A	N/A	N/A	N/A	N/A	N/A
CDWP	ppb CN^-	3.4	11.1	1.4	5.9	6.6	17
	H.T.	57h 18m	57h 19m	56h 54m	56h 55m	56h 53m	56h 54m
RWQCP	ppb CN^-	4.7	11.9	0.8	5.3	8.1	18.5
	H.T.	57h	57h 1m	56h 43m	56h 44m	56h 42m	56h 42m
WMWD	ppb CN^-	3.2	11.1	2.2	9.4	2.7	12.9
	H.T.	61h 51m	61h 52m	61h 38m	61h 39m	61h 36m	61h 37m
Preserved							
IEUA	ppb CN^-	1.1	6.9	0.9	4.6		
	H.T.	56h 59m	57h	57h 1m	57h 2m		
YVWD	ppb CN^-	1	10.1	4	13.1		
	H.T.	N/A	N/A	N/A	N/A		
CDWP	ppb CN^-	7.6	16.2	7.2	17.3		
	H.T.	56h 56m	56h 57m	56h 58m	56h 59m		
RWQCP	ppb CN^-	7.8	15.8	5.3	15.1		
	H.T.	56h 45m	56h 46m	56h 47m	56h 48m		
WMWD	ppb CN^-	2.2	12.3	2.2	12.6		
	H.T.	61h 40m	61h 41m	61h 42m	61h 42m		

Run 3. Amount of cyanide (ppb) detected in preserved and non-preserved effluent wastewater samples that were prepared for free cyanide detection and analyzed using colorimetric methods. Shaded samples were chlorinated and dechlorinated before collection. H.T.=Holding Time. N/A=Not Available. Samples were preserved to pH ≥ 11 and pH ≥ 12 with 1 M NaOH. Lead Carbonate was added to samples treated for sulfide. Spiked=5.5 ppb CN^-.

Table 9. Effluent-Total Colorimetric-Run 3

Total Cyanide Colorimetric		S^{2-} trtment	S^{2-} trtment, Spike	W/O S^{2-} trtment	W/O S^{2-} trtment, Spike	S^{2-} trtment, pH≥12	S^{2-} trtment, Spike pH≥12
Non-Preserved							
IEUA	ppb CN^-	2	5.1	N.D.	7.3	0.9	5.5
	H.T.	55h 38m	55h 39m	55h 5m	55h 6m	55h 4m	55h 4m
YVWD	ppb CN^-	1.6	5.2	N.D.	3.3	3	7.3
	H.T.	N/A	N/A	N/A	N/A	N/A	N/A
CDWP	ppb CN^-	1.1	5	N.D.	3.1	2.8	7.9
	H.T.	55h 24m	55h 25m	55h 2m	55h 3m	55h	55h 1m
RWQCP	ppb CN^-	2	5.7	N.D.	3.5	2.5	6
	H.T.	55h 8m	55h 9m	54h 51m	54h 52m	54h 49m	54h 50m
WMWD	ppb CN^-	N.D.	3.6	N.D.	3.6	N.D.	4.6
	H.T.	59h 58m	59h 59m	59h 46m	59h 47m	59h 44m	59h 45m
Preserved							
IEUA	ppb CN^-	0.9	4.3	0.6	3.2		
	H.T.	55h 7m	55h 8m	55h 9m	55h 10m		
YVWD	ppb CN^-	N.D.	4.3	N.D.	5.1		
	H.T.	N/A	N/A	N	N/A		
CDWP	ppb CN^-	3.7	7.9	2.4	7.6		
	H.T.	55h 4m	55h 5m	55h 6m	55h 6m		
RWQCP	ppb CN^-	3.3	8.2	2.6	8.3		
	H.T.	54h 53m	54h 53m	54h 54m	54h 55m		
WMWD	ppb CN^-	N.D.	4.5	N.D.	4.6		
	H.T.	59h 47m	59h 48m	59h 49m	59h 50m		

Run 3. Amount of cyanide (ppb) detected in preserved and non-preserved effluent wastewater samples that were micro distilled for total cyanide detection and analyzed using colorimetric methods. Shaded samples were chlorinated and dechlorinated before collection. H.T.=Holding Time. N/A=Not Available. N.D.=Non-detectable ($\leq$ 0.5 ppb CN^-). Samples were preserved to pH $\geq$ 11 and pH $\geq$ 12 with 1 M NaOH. Lead Carbonate was added to samples treated for sulfide. Spiked=5.5 ppb CN^-.

CHAPTER FOUR

DISCUSSION AND CONCLUSIONS

Introduction

The wastewater treatment plants in the Santa Ana Watershed are faced with a problem of how to correctly and consistently analyze cyanide. The reason is that there has been no consistent method developed in which to analyze cyanide in treated and untreated wastewater. The studies being conducted on cyanide testing focus on producing consistent, reliable, and easy methods feasible for all facilities. Due to the interferences that occur throughout the process this has not been possible. Many facilities have modified the current methods to work for their situations. Unfortunately, every facility has different situations and what works for one facility may not work for another.

This project has identified that interferences are a problem when it comes to analyzing cyanide consistently. Testing total and free cyanide using colorimetric methods and available and free cyanide using amperometric methods led to an inconsistency that may be due to interferences

that can occur during the treatment and analysis process, the small sample size, or through random error.

Distillation

There are two ways of distilling samples for cyanide analysis. The first way is by conventional "macro" distillation. This is a traditional distillation method with large pieces of connected glassware that is very time consuming and not very precise. It requires a large amount of volume (500 mL) and only two samples at a time can be distilled. In a study on distillation recoveries done in the CSUSB laboratory, macro distillation had a recovery yield of 80% $\pm$ 20%. The second way is by "micro" distillation in a small, sealed sample tube with a gas diffusion membrane, and a heating block for the tubes to fit into. This is a newer method that does not take as much time as macro distillation does and is much more precise. It requires a considerably smaller amount of volume (6 mL) and twenty-one samples can be distilled at a time. In the distillation recovery study micro distillation had a recovery yield of 96% $\pm$ 5%. It is apparent that micro distillation yields a higher and more precise cyanide recovery. It also appears that micro

distillation is better at getting rid of interference that can result in false cyanide recoveries. In this project macro distillation resulted in fifty percent of the samples from run one being non-detectable for cyanide. Micro distillation resulted in fifty-eight percent of the samples from run three being non-detectable for cyanide. Micro distillation is the obvious choice for distilling wastewater samples and should be considered when developing a uniform method for total cyanide.

Free cyanide was detected at a higher level compared to total cyanide in both the effluent and influent water samples tested using colorimetric detection. In the first run influent water samples that were macro distilled did not have any total cyanide detected $\geq$ 5 ppb CN^-. The same water samples were not distilled and had sixty-three percent of the free cyanide samples $\geq$ 5 ppb CN^-. In the second run effluent samples that were micro distilled had eight percent of the total cyanide samples $\geq$ 5 ppb CN^-. The same water samples were not distilled and fifteen percent of those free cyanide samples were $\geq$ 5 ppb CN^-. The free cyanide samples were generally higher than the total cyanide samples. This should not be the case because total cyanide encompasses the free cyanide found in

samples. The total cyanide should have higher detection compared to the free cyanide in the same sample. One explanation for this is that distillation removes the interferences that results in a lower detection of total cyanide compared to free cyanide in the sample. When the sample is not distilled there could be more interference in the sample producing a higher free cyanide analysis than what is really there.

It is apparent that distillation is an important step in eliminating interferences found in wastewater samples that cause inaccurate cyanide results. Non-distilled influent samples have a free cyanide detection of over 10 ppb CN^- and macro distilled influent samples have a total cyanide detection of less than 2 ppb CN^-. In every colorimetric method performed distillation lowered the number of cyanide samples that were over 5 ppb CN^-. Run one influent was sixty-three percent $\geq$ 5 ppb CN^- without distillation and zero percent $\geq$ 5 ppb CN^- with distillation; run one effluent was forty percent $\geq$ 5 ppb CN^- without distillation and ten percent $\geq$ 5 ppb CN^- with distillation; run two effluent was fifteen percent $\geq$ 5 ppb CN^- without distillation and eight percent $\geq$ 5 ppb CN^- with distillation; and run three effluent was forty-four percent

$\geq$ 5 ppb CN^- without distillation and zero percent $\geq$ 5 ppb CN^- with distillation. In a number of distilled samples that were analyzed the amount of cyanide was too low to be detected by FIA analysis, generally considered to be the highest sensitivity method available. In run two effluent ten percent of the total cyanide samples were non-detectable and in run three effluent fifty-eight percent of the total cyanide samples were non-detectable. It can be suggested from this data that distillation is an important step to ensure accurate results when analyzing cyanide in wastewater.

Distillation gets rid of some of the interferences that create the false cyanide readings found when the samples are analyzed without distilling. The intermediate sulfide scrubber used in the distillation process removes the sulfide which can cause interference if it is left in the samples. Free cyanide readings that are as high as 10 ppb CN^- are detecting more than just the free cyanide in the matrix when total cyanide readings are lower in the same sample collected. At some point during the distillation process the interferences that are producing higher cyanide reading are being removed.

The effluent samples gave similar results although they were lower. The non-distilled effluent samples have over 2 ppb free cyanide and the macro distilled effluent samples have less than 1 ppb of total cyanide detected. The results from micro distillation show that distillation removes more than just sulfide from the sample. The micro distilled total cyanide samples that were treated for sulfide before distillation were all lower than the free cyanide samples that were treated with sulfide and not distilled. Both samples were treated with lead carbonate to remove the sulfide and the results suggest that the distillation process may have removed other interferences.

The results from colorimetric analysis show that distillation is an important step in preventing cyanide interference. In particular, micro distillation is a more precise way to measure the total cyanide in the sample. However, WWTPs may not include this step because they may feel that it is too time consuming and does not change their results enough to be worthwhile. Some WWTPs do not analyze their own samples and have little control over the process in which it is done. Distillation is not a major concern to WWTPs because the results they get without distilling are still under the limits set forth by

regulating agencies, and without distillation free cyanide is supposed to be measured with the colorimetric method, and this is the species targeted by regulatory agencies. A problem may occur if the agencies lower the limits even further or if their cyanide levels start going up. They will probably acknowledge distillation as a big enough benefit to start using it. As of right now the problems do not outweigh the benefits for them and so they chose not to distill.

Sodium Hydroxide Preservation

There are two options for WWTPs when they go to collect and analyze their sample: run the sample immediately after collecting it or preserve the sample for analysis at a later time. Preservation is the necessary step for many WWTPs that do not have a laboratory at their facility or the time to immediately run samples. A common way of preserving the wastewater effluent and influent samples is using NaOH to raise the pH to $\geq$12. However, there are many problems associated with preservation that lead to false cyanide readings in the preserved influent and effluent samples. In the first run the preserved samples were held for a longer time than the non-preserved

samples before they were analyzed. The holding times were higher for the preserved samples because of the ability to store them before they needed to be analyzed in order to have time to macro distill the samples. With the limited resources and time available it was imperative that the non-preserved samples were macro distilled and ran immediately after collection. In comparing the preserved and non-preserved influent samples it was observed that there was a difference in the results when a sample was spiked compared to when it was not spiked. This was something that was not observed in the effluent samples. The preserved free and total cyanide samples were lower than the non-preserved samples with the exception of one sample in those that were not spiked. In comparison the preserved samples that were spiked had a higher free and total cyanide reading compared to the non-preserved samples. It is difficult to say with conviction what is occurring here especially since all of the samples in the first run were spiked to the same concentration of 12.6 ppb CN^-. The only thing that can be said with certainty is that there is an inconsistency occurring between preserved and non-preserved influent samples and whether they are spiked or not. Obviously at some point interferences are

occurring or resulting in the inconsistent results. Interferences in the preservation process may lead to these results. Perhaps the spiked cyanide that is added for control comparison is reacting with the NaOH and producing high free and total cyanide detection. The recovery precision may be poor and more samples need to be run in order to get more precise results.

Preservation increased the amount of colorimetric and amperometric free cyanide detected in non-distilled effluent samples as well as increased the amount of total and available cyanide in the samples. While the total and available samples were lower than the colorimetric and amperometric free cyanide samples there was still an increase in cyanide detection when the samples were preserved. However, it did not show an inconsistency between whether the sample was spiked or not like the influent did. The preserved samples for free cyanide amperometric analysis in run two had forty-five percent $\geq$ 5 ppb CN^- and the non-preserved samples had twenty percent $\geq$ 5 ppb CN^-. The preserved and non-preserved samples for available cyanide analysis in run two had zero percent $\geq$ 5 ppb CN^-. The preserved samples for free cyanide colorimetric analysis in run three had fifty-five percent $\geq$

5 ppb CN^- and the non-preserved samples had thirty-seven percent $\geq$ 5 ppb CN^-. The preserved and non-preserved samples for total cyanide analysis in run three had zero percent $\geq$ 5 ppb CN^-. The high number in both preserved and non-preserved amperometric and colorimetric free cyanide samples is most likely a result of the samples not being distilled to remove interferences. The higher number in the preserved samples is most likely the result of interferences that occur during preservation.

It is apparent with both the effluent and influent samples that by increasing the holding time the free cyanide detected in the sample goes up. There were a higher percentage of non-detectable samples that were not preserved than were preserved in each of the runs. This is most likely due to the opportunity for interferences to develop before analysis. Preservation increases cyanide detection for free and total cyanide analysis. This is why most WWTPs if they have an adequate testing facility will test the samples immediately without worrying about preservation. The direct effluent samples analyzed in run one, increased by 1 ppb CN^- in two days and over 4 ppb CN^- in one week of preservation. In runs two and three, the effluent samples increased on average by 1 ppb CN^- after

about twelve hours of preservation. This can result in problems for the WWTPs that have to preserve their samples to be tested at another facility or don't have enough time to analyze the samples after collection.

pH

When preserving a sample the correct pH level needs to be used. Several methods suggest pH $\geq$ 12 for preservation of the samples and some methods suggest pH $\geq$ 11. This project preserved samples using both pH levels to determine if one is better than the other at preventing interferences. The total cyanide level was lower in samples that were preserved at pH $\geq$ 12 and treated for sulfide compared to samples that were preserved at pH $\geq$ 11. The free cyanide level was higher in samples that were preserved at pH $\geq$ 12 and treated for sulfide compared to samples that were preserved at pH $\geq$ 11. This data suggests that it is better to preserve the samples at pH $\geq$ 12 when analyzing total cyanide and when analyzing free cyanide it is better to preserve the samples at pH $\geq$ 11. Further analysis needs to be done in order to fully accept these findings.

Chlorination and Dechlorination

WWTPs have a number of ways that they can purify their water. Chlorination and dechlorination is commonly used to kill bacteria and other contaminants in wastewater. While it does a good job at getting rid of the bacteria and contaminants it is thought to create interferences that lead to false cyanide detection in wastewater samples. The data suggests that preserved samples that are chlorinated and dechlorinated have a higher amount of cyanide detected compared to samples that are not chlorinated and dechlorinated. In effluent amperometric free cyanide run two the preserved chlorinated and dechlorinated sample was sixty-three percent $\geq$ 5 ppb CN^- and the preserved sample that was not chlorinated and dechlorinated free cyanide sample was thirty-three percent $\geq$ 5 ppb CN^-. The non-preserved samples that are chlorinated and dechlorinated are lower than the non-preserved samples that were not chlorinated and dechlorinated. In effluent amperometric free cyanide run two the non-preserved chlorinated and dechlorinated sample was zero percent $\geq$ 5 ppb CN^- and the non-preserved sample that was not chlorinated and dechlorinated was thirty-three percent $\geq$ 5 ppb CN^-. These results show that the preservation process and the

chlorination and dechlorination process create interferences that lead to false cyanide readings. It appears that a high pH is required with the dechlorination reactants or products in order to create the interference. WWTPs that chlorinate and dechlorinate should be careful when preserving their samples. The best method is to perform immediate analysis after chlorination and dechlorination without adjusting the pH in order to prevent interference from developing.

Sulfide Treatment

Sulfide is an interference that is thought to cause false CN^- readings when it is not removed from the sample. Most methods recommend removing sulfide from the sample before analysis. In the non-preserved samples treated for sulfide the majority of the WWTP samples were higher than samples not treated for sulfide. In the preserved samples the majority of the WWTP samples were higher than samples not treated for sulfide. The addition of lead carbonate as a treatment for sulfide may be causing an interference in the sample. Further studies are required to determine if this is the case. If lead carbonate is creating an interference, other ways to treat for sulfide should be

pursued. Lead sulfide can react with thiocyanate releasing free cyanide *(8)*. This may be the reason for higher free CN^- detections in the samples treated for sulfide. Effluent samples are treated samples unlike influent samples which is why the results may be lower. They have gone through a treatment process that has made them suitable to discharge into the Santa Ana River. Unfortunately, this process still allows for interferences to occur in the samples.

Conclusion

The results from this project imply that distillation lowers false cyanide amounts detected in samples while preservation, sulfide treatment, and chlorination/ dechlorination increases them. If WWTPs are having problems staying within the cyanide regulations and guidelines they should distill if they have to preserve their samples. They should also distill their samples if they have to preserve samples that have been chlorinated and dechlorinated. There are a number of steps within the treatment and analysis process where interferences can occur which can create many problems. The majority of the

blank data does not show appreciable cyanide concentrations suggesting that there is matrix interference.

Interferences may be causing the inconsistent results. Unfortunately, due to time constraints this project was unable to determine the statistical significance of the interferences that have been suggested and can only be inferred at this time. In the future the statistical significance of this data should be analyzed. Additional studies need to test more samples and focus on finding out exactly where the problems are occurring and how to prevent them.

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