Problems Associated with Using Current EPA Approved Total Cyanide Analytical Methods for Determining Municipal Wastewater Treatment Plant NPDES Permit Compliance

Ben D. Giudice, M.S., Brant Jorgenson, Michael Bryan, Ph.D.[1]

[1] Corresponding author. Managing Partner, Robertson-Bryan Inc., 9888 Kent St, Elk Grove, CA 95624 (916) 714-1802

ABSTRACT

Many municipal wastewater discharges currently exceed total cyanide (CN) effluent limitations when based on analytical results from standard EPA methods. The approved EPA methods used to measure CN in wastewater effluent are prone to numerous interferences that are unpredictable and difficult to mitigate. Substantial evidence indicates that these analytical problems are causing many current CN compliance issues, rather than actual high CN concentrations in the treated effluent. The preservative NaOH is required to be added to all samples that cannot be analyzed in less than 15 minutes, and NaOH is itself a proven interference for which there is no specific mitigation technique. Substantial evidence suggests NaOH addition may be unnecessary to maintain sample integrity over typical hold-times prior to analysis. Based on this information, CN measurements made under the current paradigm are likely inaccurate and produce unreliable information for determining NPDES permit compliance.

INTRODUCTION

The National Toxics Rule (NTR) established a cyanide (CN) freshwater aquatic life chronic criterion of 5.2 µg/L (USEPA 1992). With no dilution credit, the procedure outlined in the *Policy for Implementation of Toxics Standards for Inland Surface Waters, Enclosed Bays, and Estuaries of California* (SIP) results in average monthly effluent limit (AMEL) of 4.1 µg/L. Per the SIP, NTR compliance is required by May 18, 2010 (SWRCB 2005). Neither the 5.2 µg/L criterion nor the 4.1 µg/L effluent limit can consistently be met by all dischargers. This problem affects multiple Central Valley municipal wastewater dischargers with various treatment systems. Substantial evidence exists to indicate that effluent measurements of CN above these limits are due to analytical interferences and do not accurately reflect true effluent CN concentrations, which may be well below these limits.

CYANIDE SOURCES AND SPECIATION

Cyanide can be found in wastewater influent and is usually a result of industrial discharges. Pretreatment for the removal of CN is usually practiced for industrial sources, so influent concentrations are generally very low. Nevertheless, CN is often measured at high concentrations in effluent, often exceeding measured influent concentrations (WERF 2003). Potential causes of this phenomenon include CN generation from CN precursors during disinfection (both chlorination and UV processes), as well as analytical interferences, which are discussed in detail below.

Cyanide exists in a variety of forms. It can be free or part of strong or weak complexes with other species. The analytical method employed determines what type of CN is measured; all CN measurements are method determined. Types of CN measured include: total, available, amenable to chlorination, weak acid dissociable, free, and others. Cyanide species vary in their environmental fate and transport and toxicity to aquatic life. Permits typically require analysis of total CN, but aquatic life criteria are based on free CN, the primary toxic form (EPA, 1985).

CYANIDE ANALYSIS AND INTERFERENCES

Many methods exist for the analysis of CN in wastewater (some approved and some not approved by EPA), but for NPDES permit compliance monitoring, dischargers almost universally utilize acid distillation procedure with amperometric or spectrophotometric detection yielding a total CN measurement (i.e., EPA methods 335.2, 335.4, and 9010B, Standard Method 4500-CN). Developed for the mining industry, which typically sees CN concentrations more than three orders of magnitude higher than in municipal wastewater effluents, distillation-based methods have been employed in cyanide analysis for decades with little modification to their overall procedure.

Complex CN chemistry leads to numerous potential interferences that have been documented for this method both in practice and in the scientific literature. For some time, and particularly within the last decade, considerable research has been directed at understanding and managing the many confounding interferences that make the distillation methods problematic, particularly when attempting to quantify cyanide at single-digit part-per-billion concentrations. Compounds that can interfere with accurate CN measurement include aldehydes, carbonates, nitrite, nitrate, oxidants, sulfide, sulfur compounds, and thiocyanate (USEPA 2007, ASTM 2009, WERF 2003, Carr 1997, Delaney 2007, Weinberg 2005). The magnitude and direction of potential bias is not well understood. If present in a collected sample, the addition of various “stabilizing” chemical reagents or procedures at the time of sample collection and/or analysis is required by the many footnote additions in EPA’s last rulemaking regarding preservation and stabilization techniques for cyanide analysis (USEPA 2007). The numerous analytical interferences and complex mitigation procedures, which themselves may create interferences, create serious difficulties for the regulated community. Furthermore, EPA notes: “There may be interferences that are not mitigated by approved procedures” (USEPA 2007, footnotes to Table II). This lack of confidence is most troubling when CN measurements submitted as part of NPDES permit monitoring programs may be used for imposing monetary fines, issuing cease and desist orders, and driving construction of modified treatment facilities.

It is important to note here that these analytical errors are not related to poor sampling or human error, but rather are the expression of inherent vulnerability in the distillation-based analytical procedure. A review of the analytical standard operating procedure demonstrates the many if/then clauses that render the methods prone to such error and lend understanding to EPA’s statement “There may be interferences that are not mitigated by approved procedures.” It is difficult to rely on such a system of analysis to consistently produce accurate and precise results. The EPA and standards setting organizations, such as ASTM International and Standard Methods, have acknowledged shortcomings in approved methods and are engaged in updating and revising standard approved analytical procedures.

PRESERVATION WITH SODIUM HYDROXIDE

In 40 CFR 136, Table II, the addition of the preserving agent sodium hydroxide (NaOH) is required to adjust the pH of the sample to > 12 if the sample cannot be analyzed within 15 minutes. The original purpose of requiring the addition of NaOH was to extend the hold-time, since CN was assumed to volatilize quickly at neutral pH, thereby losing the CN in the sample prior to its measurement. With the addition of NaOH, the specified hold-time is 14 days (USEPA 2007). However, NaOH has itself been shown to be an interferent. Sample handling and manipulation techniques designed to mitigate other interferences may be partially effective, but NaOH is always required to be added to samples, which universally introduces a potential interference for which there are no specific mitigation techniques.

For example, a study performed by the Los Angeles County Sanitation Districts examined whether pH adjustment through the addition of NaOH and/or common dechlorination agents resulted in increased CN concentrations. Immediate analysis without addition of NaOH generally resulted in total CN concentrations below the reporting limit (5 µg/L). With the addition of NaOH, a slight to significant increase in CN concentration was observed, depending on the dechlorinating agent used (Figure 1). The results are evidence that addition of NaOH produces artificially high CN concentrations in wastewater effluent matrices (Khoury 2008).

Central Valley dischargers have conducted similar studies with similar results. The City of Roseville has conducted analyses of total CN on split samples of wastewater effluent, one preserved with NaOH and one unpreserved. The time between sample collection and analysis for the experiments was 1-2 hours. In all cases at both plants operated by the City of Roseville, preservation of samples gave higher CN concentrations, often more than double the concentration measured in the unpreserved sample (City of Roseville 2009). The City of Vacaville conducted similar experiments, analyzing split samples of wastewater effluent, one preserved with NaOH and one unpreserved. In these experiments, the time between sample collection and analysis was < 15 minutes. Preservation of samples resulted in average concentrations 427% higher than unpreserved concentrations. With preservation, 82% of the measurements greater than effluent limits, while only 5% of unpreserved samples were above effluent limits (City of Vacaville 2008). Results from the Roseville and Vacaville studies are presented in Figure 2.

The above study results are strong evidence that NaOH is positively biasing CN measurements. Taken alone, however, it would also be theoretically possible that omission of NaOH as a preservative results in volatilization (i.e., loss of) CN prior to measurement, leading to lower concentrations in unpreserved samples. However, evidence indicates that CN in unpreserved wastewater effluent samples does not volatilize quickly. For example, a study conducted by the City of San Jose showed higher CN concentrations in preserved samples than in unpreserved samples and investigated whether CN in unpreserved samples was volatilizing (i.e., being lost) prior to analysis. The results confirmed that this was not the cause of lower CN concentrations in unpreserved samples (City of San Jose 2004). In the same study, a hold-time assessment showed CN concentrations were stable for at least 14 days in multiple matrices with varying initial CN concentrations (Figure 3; City of San Jose 2004). Hold-time studies conducted by ASTM International on municipal wastewater treatment plant effluent and in an artificial effluent matrix resulted in maximum allowable hold-times of unpreserved samples greater than 14 days and greater than 6 days for available CN and aquatic free CN tests, respectively (ASTM 2009). Additionally, preliminary results from a hold-time study conducted by the City of Vacaville indicate very stable total CN concentrations for greater than 7 days in unpreserved samples (City of Vacaville 2010).

EPA acknowledges these challenges and is considering amendments to 40 CFR 136 that provide explicit guidelines on eliminating NaOH as part of the method. In lieu of or in addition to existing guidelines, EPA has proposed the adoption of cyanide preservation procedures detailed in ASTM Standard Practice D7365-09a. D7365-09a specifies that users should conduct a hold-time study prior to elimination of NaOH. Once the hold-time study is complete, NaOH may be omitted as a preservative as long as the sample is analyzed within the determined hold-time (ASTM 2009, Walker 2009).

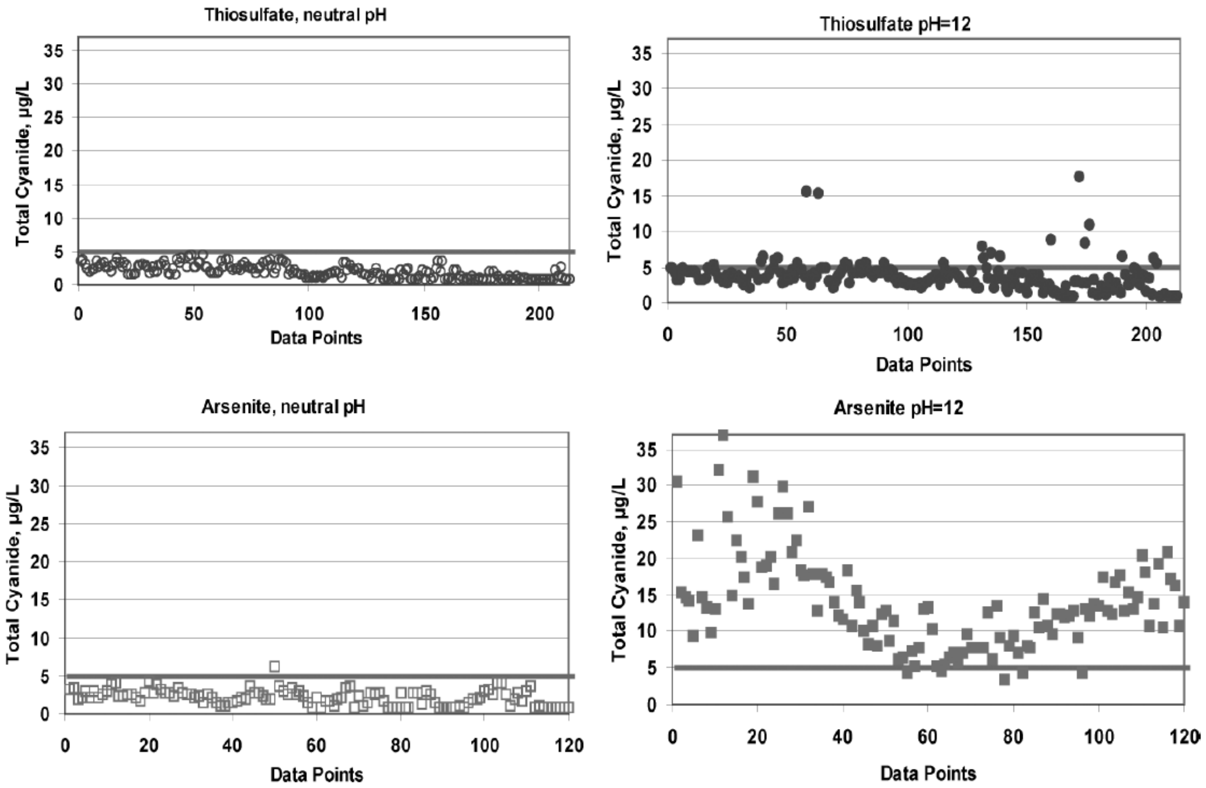

Figure 1. Total cyanide results for two chlorine quenching agents and two preservation methods for split samples compiled from Los Angeles County Sanitation District's San Jose Creek East, San Jose Creek West, Valencia, and Saugus Water Reclamation Plants. 5 µg/L is the reporting limit. The x-axis is an arbitrary labeling of data points (reproduced from Khoury 2008).

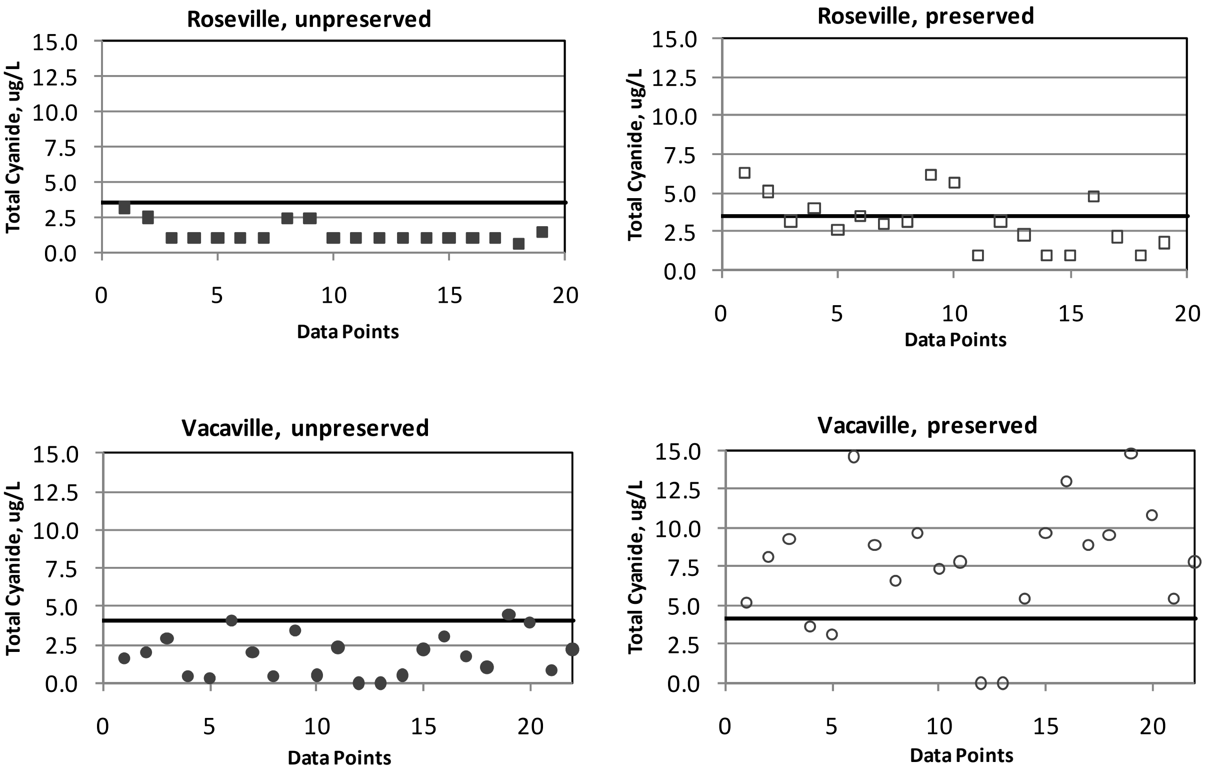

Figure 2. Total cyanide results for side-by-side analyses of split samples, one preserved with sodium hydroxide (NaOH) and the other unpreserved, from the City of Roseville's Pleasant Grove and Dry Creek Wastewater Treatment Plants (hold-time is 1 to 2 hours) (City of Roseville 2009) and the City of Vacaville's Easterly Wastewater Treatment Plant (hold-time is less than 15 minutes) (City of Vacaville 2008). The average monthly effluent limit for Vacaville and Roseville are 4.1 µg/L and 3.5 µg/L, respectively. The x-axis is an arbitrary labeling of data points.

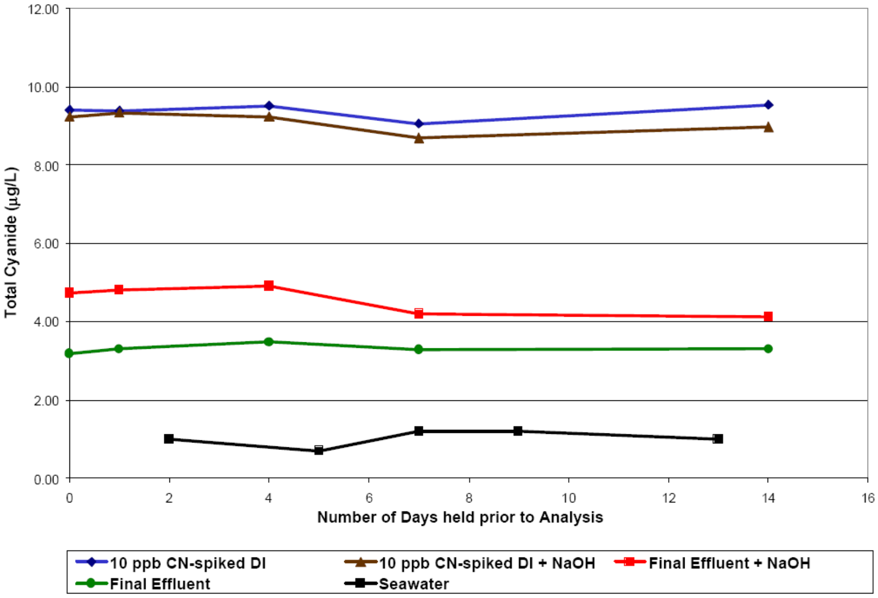

Figure 3. Hold-time study using de-ionized (DI) water, ambient seawater, and San Jose/Santa Clara Water Pollution Control Plant effluent with and without NaOH Preservation (reproduced from City of San Jose 2004).

LITERATURE CITED

ASTM International. 2009. Standard Practice for Sampling, Preservation and Mitigating Interferences in Water Samples for Analysis of Cyanide. D7365-09a.

Carr, S., R. Baird, B. Lin. 1997. Wastewater derived interferences in cyanide analysis. *Water Research*. 31: 1543–1548

City of Roseville. 2009. Unpublished data.

City of San Jose. 2004. *Cyanide Attenuation Study*. Investigations and Laboratory Staff Watershed Protection Group, Environmental Services Department.

City of Vacaville. 2008. Unpublished data.

City of Vacaville. 2010. Unpublished data.

Delaney M., C. Blodget, C. Hoey, N. McSweeney, P. Epelman, S. Rhode. 2007. False cyanide formation during drinking water sample preservation and storage. *Environmental Science & Technology*. 41: 8383-8387

Khoury et al. 2008. Cyanide Generation During Preservation of Chlorinated Wastewater Effluent Samples for Total Cyanide Analysis

SWRCB (State Water Resources Control Board). 2005. *Policy for Implementation of Toxics Standards for Inland Surface Waters, Enclosed Bays, and Estuaries of California*.

USEPA. 1985. Ambient water quality criteria for cyanide – 1984. EPA 440/5-84-028. Washington DC.

USEPA. 1992. Water quality standards; Establishment of numeric criteria for priority toxic pollutants; States' compliance. Final Rule. *Federal Register*. 57: 60848.

USEPA. 2007. Guidelines establishing test procedures for the analysis of pollutants under the Clean Water Act; National Primary Drinking Water Regulations; and National Secondary Drinking Water Regulations; analysis and sampling procedures. Final Rule. *Federal Register*. 72: 11200-11249.

Walker, Lemuel. U.S. Environmental Protection Agency. 2009. Personal Communication.

WERF (Water Education Research Foundation). 2003. *Cyanide formation and fate in complex effluents and its relations to water quality criteria*. WERF No. 98-HHE-5. Alexandria, VA.

Weinberg H., S. Cook, P. Singer. 2005. Insights to false positive total cyanide measurements in wastewater plant effluents. *Water Environment Research* 77: 491–499