

Segmented Flow Injection, UV Digestion, and Amperometric Detection for the Determination of Total Cyanide in Wastewater Treatment Plant Effluents

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The currently approved method for the analysis of total cyanide (TCN) in wastewaters has remained virtually unchanged in the 25 years since its initial use; this despite its subjection to a number of interferences, many of which provide a positive bias in cyanide measurements, including the formation of TCN during sample processing and some of which remain undocumented to this day. In particular, many municipal wastewater treatment plant chlorinated effluents throughout North America have often been cited for permit violations on the levels of total cyanide in their effluents measured using this methodology. A recently developed procedure for the analysis of TCN in various matrixes that utilizes segmented flow injection for sample transport and reaction, on-line acidic UV digestion for conversion of complexed cyanide to HCN, and amperometric detection achieved within 4 min of sample injection is demonstrated on chlorinated effluents discharged from municipal wastewater treatment plants. Through a systematic evaluation of the chemistry of the processes involved in this method and an understanding of the complexity of the wastewater matrix, an application was developed that showed consistent reproducibility in measuring TCN in a variety of effluents. The method was employed initially on synthetic solutions containing controlled levels of constituents identified in the literature as interfering with the measurement of TCN through the traditional distillation/colorimetric approach. In its application to the analysis of TCN in chlorinated wastewaters, an approach was evolved that ensured that dechlorination carried out during sample processing did not bias the results of analysis.

Cyanide Chemistry. An increasing number of publicly owned treatment works are reporting difficulties in complying with permits for total cyanide (TCN) levels in effluent discharges, and some are facing legal action by public challengers as a result of being unable to control these “apparent” permit violations. Part of this problem is the impossible burden placed on utilities and

their contract analytical laboratories to determine cyanide levels often at or below the practical quantitation limit set by the United States Environmental Protection Agency (EPA) at 10 $\mu\text{g/L}$ for the currently approved analytical methodology.¹ In addition, the methodology is cumbersome, unreliable, and in many cases, fails to effectively recover measured additions of cyanide in the matrix being analyzed.² Moreover, there have been instances of “apparent” levels of cyanide in the chlorinated effluents of plants that had no measurable level at any other point during treatment. It is clear that an alternative technique to the existing EPA-approved methodologies should take advantage of modern separation techniques that use automation and provide for rapid sample throughput with minimal sample handling while readily achieving reliable detection of cyanide well below the regulated levels.

The chemistry of cyanide, which includes all of the CN groups that can be determined as the cyanide ion,³ has been long studied for its toxic effects to humans and the environment. At pH values below the $\text{p}K_a$ (9.21^{4,5}), which would be the pH of natural waters and wastewaters, the dominant form of free cyanide is, therefore, the volatile hydrogen cyanide.

The cyanide molecule can also act as a ligand to bind with metal ions to form stable complexes,⁶ the stability of which depends on the type of metal and its oxidation state. Metals that can become a part of this complex include cadmium, lead, nickel, zinc, and iron.⁷ Yet most of these complex forms are very stable, thus rendering them virtually nontoxic, the exception being the iron complexes, which can undergo photolytic decomposition.⁸ The relationship between the complex species and the free species

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- (2) Federal Register. *Guidelines Establishing Test Procedures for the Analysis of Cyanide Under the Clean Water Act*. U.S. Government Printing Office: Washington, DC, 1995; Vol. 60(228), p 60650.
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nevertheless depends on the pH and metal concentrations. The dominant cyanide species in municipal wastewater are the metal complexes. A study listing various domestic wastewater treatment plant raw wastewater cyanide speciation found that 74–83% of the total cyanide was of the complexed form,⁷ with the remaining fraction being the free form. This speciation is similar to that found in unpolluted natural waters.⁹

Analytical distinction of the different classifications of cyanide is difficult to perform, and because of this, cyanide concentrations are often reported in terms of total cyanide (TCN), which is the sum of free, simple, and complex cyanide,³ and which is often used as the basis for regulation in environmental matrices.

Approved Analytical Methods for Total Cyanide Analysis in Wastewaters. The most commonly employed method for total cyanide analysis in wastewater is described in Standard Method 4500-CN⁻,³ American Society for Testing and Materials method D2036-97¹⁰ and EPA method 335.2¹. The manual procedure separates cyanide from the aqueous sample by the use of a high-temperature, low pH distillation reactor to break down all the complex cyanides into HCN. A major disadvantage of this procedure is the long sample analysis times, typically 1.5–2 h per sample, which makes quality assurance and quality control very difficult to administer. Hence, spikes and duplicates of samples that add significant amounts of run time to the complete analysis of samples are rarely carried out. Furthermore, many safety concerns arise for the laboratory personnel, since a variety of toxic chemicals and hazardous conditions are present. Precautions such as performing this analysis in a hood and requiring that all personnel wear protective clothing can help to alleviate this danger; however, complete protection of personnel is not possible.

Another approach for total cyanide analysis, listed as EPA method 335.3¹ and in a new draft international standard (ISO/DIS 14403),¹¹ is an automated, ultraviolet digestion technique that employs the same chemistry as the Standard Method, but is set up as a flow injection system. This particular method uses some of the same chemicals as the manual method, and although reducing the sample run time and operator intervention, this method, depending on instrument configuration, sometimes has trouble with the stabilization of the flow through the colorimetric cell, and various irregularities have been reported with sample analysis.¹² These stem in part from the multiple postdigestion reaction feeds required to take the free cyanide through the complexation steps prior to analysis. False positive bias has been demonstrated from the photodegradation of ubiquitous thiocyanate in the UV reactor.¹³

Documented Interferences in Analysis Using Approved Methodologies. *Sulfide.* Sulfide is the most reduced form of sulfur in wastewater. It is usually present in anoxic waters as a result of

the presence of sulfate-reducing bacteria. Sulfide is a diprotic acid that has the same pH dependence of solubility as free cyanide. This allows it to volatilize and carry over with the cyanide in the Standard Method, subsequently interfering with the colorimetric measurement by suppressing the desired complexation reactions. In addition, sulfide and other sulfur compounds can react with cyanide to form thiocyanate, which is not captured as total cyanide and would therefore cause a negative bias in total cyanide measurement if this were to occur during sample handling and analysis.³ The suggested approach for sulfide removal from wastewater is the use of an agent that will precipitate the sulfide as an insoluble form, which can then be removed through filtration with a 0.45- μ m filter. One such agent is lead carbonate, whose solubility product¹⁴ at 25 °C is $1.5 \times 10^{-13} \text{ mol}^2 \text{ L}^{-2}$. The dissolved lead species engages the sulfide in a reaction with equilibrium constant $10^{-28} \text{ mol}^2 \text{ L}^{-2}$. These reactions will result in sulfide removal from the sample, since the precipitated form of sulfide is physically removed from the sample by filtration. Only an extremely small amount of sulfide will remain in solution, which corresponds to the concentration of dissolved sulfide that will be in equilibrium with the precipitated form. The Standard Method indicates that the presence of sulfide can be identified by lead acetate strips. However, these strips are inadequate for detection of sulfide below 1 mg/L, and it is thus very likely that routine analysis does not treat for sulfide removal. Its presence in samples analyzed by the Standard Method can result in a variable outcome for TCN measurement, depending on which of the mechanisms described here occur during sample treatment.

Nitrite. Nitrite is an intermediate product of nitrification and denitrification that is associated with the oxidation and reduction cycling of nitrogen in the environment.¹⁵ Some studies have suggested that nitrite may be involved in a cyanide formation reaction with certain components of wastewater.^{16,17} In particular, when Carr et al.¹⁶ chlorinated a synthetic water comprising ammonia and subsequently used ascorbic acid to quench residual chlorine, they measured elevated levels of cyanide and nitrite that were not present when one of these components was absent. However, if the order of the chemical addition was changed, neither cyanide nor nitrite was detected. A correlation was therefore found between nitrite (or other source of nitrogen) concentration, subsequent chlorination, and the use of ascorbic acid as the quenching agent (a source of carbon for the cyanide). Ascorbic acid is the most common quenching agent because of its nontoxicity during handling.

The approved procedure for removal of nitrite in the Standard Method is the addition of sulfamic acid to the sample immediately before analysis³. Nitrite in a strongly acidic solution, such as is present during distillation of the wastewater in preparation for cyanide analysis, can protonate to nitrous acid. This protonated form of nitrite has been hypothesized to be responsible for cyanide

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formation¹⁷ but since this would occur only during distillation, the need to remove the nitrite is not required by Standard Method 4500-CN until immediately before analysis rather than at the time of sample collection. On the basis of the observations of Carr et al.,¹⁶ this would not prevent the formation of cyanide during the prescribed dechlorination procedure.

Residual Chlorine. For the analysis of postchlorinated wastewater plant effluents, the Standard Method calls for the removal of any residual chlorine present in the sample.³ Approved, so-called chlorine quenching agents include ascorbic acid, sodium thiosulfate, and *m*-arsenite (NaAsO_2), which must be added in sufficient quantity so that all the residual chlorine is removed from the sample. Problems with the use of ascorbic acid were described in the previous paragraph. Chlorination at elevated pH is one method for removal of cyanide from industrial effluents, so it is expected that some soluble free cyanide in chlorinated plant effluents would be converted to cyanate and would not be captured by the TCN measurement. Residual chlorine, however, can decompose many forms of cyanide in the wastewater samples³ while collected samples are being processed and analyzed. This makes the removal of the residual chlorine imperative so that the true TCN concentration can be captured in the collected sample. However, it is far from clear that current approaches for doing so do not compromise accurate TCN measurement.

Evaluation of an Alternative Procedure for Total Cyanide.

It is clear that the existing methodology presents little opportunity to perform a large number of single analyses at one time. At over 1 h per digestion, a large number of stills would be required to generate a reasonable sample throughput. Moreover, once the complexation is carried out, spectrophotometric analysis has to be carried out without delay. To successfully determine the impact of matrix components on cyanide analysis, it is necessary to be able to carry through a large number of analyses at the same time. These should include the test samples as well as the calibration curves and spike recovery samples. With this in mind, we evaluated an alternative segmented flow injection procedure for the analysis of total cyanide in wastewaters that offers the following advantages:

- (i) Sample handling is minimized, since the sample is automatically injected into a segmented flow injection system.
- (ii) Release of free cyanide by UV radiation is contained and its subsequent detection takes place in a single sealed unit, thus removing the need for the overly vigorous acid distillation.
- (iii) Sample analysis time from sample injection to analyte response is <4 min.

The motivation to utilize this methodology came from the ability to implement more completely the objectives of quality assured analysis. The fewer sample handling stages inherent in this new procedure reduced the likelihood of external source contamination or loss of sample integrity. Flow injection analysis (FIA) is not new to the area of cyanide analysis. It is an integral part of an existing EPA methodology, an alternative to traditional distillation/colorimetry (EPA method 335.3), that uses a combination of UV and distillation but completes the analysis using the same traditional colorimetric method. Flow injection has also been proposed for the analysis of free and weakly dissociable cyanides in aquatic matrixes as OIA Method 1677.¹⁸

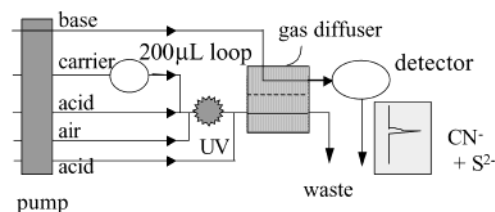


Figure 1. Scheme for flow injection method for the analysis of total cyanide.

This paper discusses the application of a recently developed alternative approach^{19,20,21} to the measurement of TCN in chlorinated wastewaters. This methodology uses an optimized UV wavelength shown to maximize release of free cyanide from most metal complexes. Acidified as HCN, the total cyanide fraction from the sample passes through a hydrophobic membrane in a gas diffuser in the presence of a basic acceptor solution to permit separation of cyanide from other components in the sample. The cyanide then passes through a low-dead-volume flowcell, where it is measured amperometrically at a silver working electrode set at a BIAS potential optimized for maximum cyanide sensitivity. A schematic representation of this methodology is illustrated in Figure 1.

One major drawback with this system is that sulfides in the aqueous sample would be converted to hydrogen sulfide in the digester and codiffuse with hydrogen cyanide into the flow cell. Sulfide and cyanide can then coelute as a single amperometric response in this methodology, thus necessitating sulfide removal from the aqueous sample prior to analysis if accurate cyanide quantitation is to be assured. The previous documented applications of this method have been to cyanide determinations in industrial wastes, not to chlorinated municipal wastewaters. The levels of total cyanide in each of these matrixes are so disparate that demonstration of effectiveness in the former cannot automatically be extrapolated to the latter, in which levels of TCN below $10 \mu\text{g/L}$ are expected. Moreover, with the demonstrated chlorination interference with the traditionally applied methodology described earlier, the FIA procedure needed to be evaluated and adapted for application in the monitoring of wastewater treatment plant discharges. This application and development are described in this paper.

EXPERIMENTAL SECTION

Flow Injection Procedure. The CNSolution 3202 (Alpkem, Wilsonville, OR) flow injection analyzer was used for total cyanide concentration determinations as outlined in Figure 1. The aqueous sample, contained in 10-mL glass test tubes held in an auto-sampler, was first loaded into a 200- μL sample loop and then switched in-line with a water carrier solution at 0.6 mL/min, producing a segmented plug of sample within the carrier solution

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stream. The sample was then acidified (1 M H_2SO_4 /0.19 M H_3PO_2), aerated, and then irradiated at 312 nm by a 4 W ultraviolet lamp with an optical path length of 960 cm created by PTFE tubing of 0.8-mm i.d. coiled around two lamps connected in series. At this wavelength, complex cyanides are converted into free cyanide, and the metal cyanide complexes are decomposed into free cyanide in the digester. Thiocyanate is left unchanged because of the use of borosilicate Pyrex glass in the reactor, which filters out the incident wavelengths that would otherwise cause photo-induced decomposition into free cyanide. The sample leaving the digester was further acidified in the presence of bismuth nitrate to convert the free cyanide into volatile hydrogen cyanide, which then passed through a gas-diffusing membrane, where the gas rose to separate from the carrier solution. The hydrogen cyanide then joined another stream of base reagent (0.1 M NaOH at a flow rate of 0.6 mL/min), which converted the volatile hydrogen cyanide into the soluble cyanide ion (CN^-). This stream passed into an amperometric detector (Dionex Corporation, Sunnyvale, CA) containing a silver working electrode and stainless steel counter electrode optimized for cyanide analysis by setting the applied potential at the working electrode to 0.16 V relative to the silver/silver chloride reference electrode (1 M NaCl). The response of the detector was continuously monitored by a computer and was graphically represented as a peak on the output showing resulting current (pA) as a function of time. The bismuth nitrate included in the second acid stream (which flowed at 0.4 mL/min.) was designed to remove up to 50 mg/L sulfide prior to entering the gas diffuser.

Cyanide stock solutions were purchased from commercial suppliers (Inorganic Ventures, Inc., Lakewood, NJ) and used to prepare calibration standards and matrix spike solutions. All sample and standard preparation was carried out in a well-ventilated hood by trained personnel wearing protective clothing, gloves, and face and eye protection to prevent exposure to toxic cyanide products. Glassware for preparation of standards (Laboratory Supply Distributors Corp., Mt. Laurel, NJ) and high-density polypropylene sample bottles for sample collection (Fisher Scientific, Pittsburgh, PA) were acid washed (10% nitric acid), triple rinsed in deionized laboratory grade water (LGW) (Dracor Inc, Durham, NC), and dried prior to use. The flow injection analyzer instrument supplies and reagent solutions were obtained from Alpkem (Wilsonville, OR). Because HCN is produced in a closed system and then converted back into a dilute basic solution during analysis, the waste from the detector effluent and the lower part of the digester were collected in separate high-density polypropylene 1-L bottles and disposed of separately. The detector cell effluent containing cyanide salts was collected by representatives of on-site Health and Safety and handled according to Federal Occupational Safety and Health Administration protocols.

Acid Distillation and Colorimetric Procedure. The separation of HCN from free and complexed cyanides in the samples was catalyzed by strong acid distillation. At basic pH, the recovered free cyanide then underwent conversion to cyanogen chloride by reaction with chloramine-T, and this product of free cyanide was then added to a complexing reagent mixture (pyridine-barbituric acid), which generated a spectrophotometric response proportional to its concentration. The complete method followed that described by Standard Method 4500- CN^- .³

Wastewater Sample Collection. Samples for analysis by the traditional acid distillation method were collected in 1-L polypropylene or linear polyethylene containers by a grab technique and preserved at pH 12–12.5 at 4 °C in the dark until analysis, preferably within 48 h of collection. The utilities had various numbers of municipal wastewater treatment plants practicing a combination of postchlorination and UV disinfection. Utility H had three; utilities A, C, and D had two each; and utilities B, E, and F had one each. These plants are denoted as A1, A2, etc. The discharge permit for most of these wastewater treatment plants is 5 $\mu\text{g/L}$ total cyanide, the exceptions being C1 and C2 with a permit of 10 $\mu\text{g/L}$.

Wastewater samples were collected at three different points in the wastewater treatment process: from the secondary clarifier effluent prior to disinfection (labeled predisinfection), from the midpoint of the contact chamber, and after disinfection (postdisinfection). These samples were preserved at pH 12–12.5 with NaOH and split for analysis by various methods and different laboratories (UNC and two state-certified laboratories, lab 1 and lab 2). For the comparative study, samples received at UNC were treated with lead carbonate to precipitate out soluble sulfides. At labs 1 and 2, the lead acetate strips were used to indicate no detectable sulfide, and hence, their samples were not treated in this way. Lab 1 provided their own sample bottles with ascorbic acid as quenching agent, the reagent used for their routine analysis procedures. UNC prepared their own sample bottles and those for lab 2, both of which contained sodium *m*-arsenite as quenching agent, once this was shown to provide the least biased outcome.

RESULTS AND DISCUSSION

The experiments described in this paper were designed to meet several objectives:

- (i) Evaluation of the applicability of FIA-UV-amperometric detection for analysis of TCN in chlorinated wastewaters,
- (ii) Comparison of the effectiveness of the FIA method relative to acid distillation,
- (iii) Determination of appropriate sample treatment processes to ensure capture of true TCN levels in chlorinated waters, and
- (iv) Application of the FIA methodology with rugged quality assurance and control (QA/QC) practice to determine limitations with existing applications and develop strategies to produce a rugged methodology.

Calibration Curve and Detection Limit with FIA. To determine total cyanide concentrations in wastewater samples, a relationship between the response of the FIA instrument and a given total cyanide concentration was developed in both LGW and the wastewater. A six-point calibration curve (2–30 $\mu\text{g/L}$ TCN as CN^-) was analyzed by the flow injection. Total cyanide solutions were prepared in 0.1 M NaOH from a stock solution (50% w/w, Fisher Scientific, Fair Lawn, NJ) containing both free (48 mg/L) and complexed (54 mg/L) cyanide (Inorganic Ventures, Inc., Lakewood, NJ) in the form of $\text{K}_4[\text{Fe}(\text{CN})_6]$, thus producing a total cyanide concentration of 102 mg/L. The recovery of free cyanide from the complexed form was determined to be 99.5% at 2 $\mu\text{g/L}$ and 99% at 30 $\mu\text{g/L}$. To determine if accurate measurements of TCN in wastewaters can be made from a calibration in a synthetic matrix, calibration curves were prepared in both LGW and a

chlorinated wastewater for plant A1. A high pH solution is needed, since cyanide is volatile at pHs below the pK_a (9.2). The response of the cyanide analyzer for known calibrant concentrations was plotted against the calibrant concentration. A best-fit regression line was determined from the data, and the mathematical equation of this line was then used to determine the total cyanide concentration of the samples. A statistical evaluation of the methodology when applied to the wastewater indicates that the analysis of the unspiked deionized water and wastewater produced a virtually indistinguishable response. Precision even at the lower end of the calibration range is very tight (<10% coefficient of variation), and the linear regression coefficient ($r^2 = 0.989$) is quite consistent from run to run and batch to batch. At 5 $\mu\text{g/L}$, the experimental bias ($-0.95 \mu\text{g/L}$) is less than the computed value ($-1.73 \mu\text{g/L}$), and hence, the presence of bias has not been demonstrated. For a wastewater matrix, this linearity, precision, and lack of bias is quite remarkable given the number of potential interferences. The method sensitivity and reproducibility are, in part, due to the successful and complete isolation of the free cyanide from the wastewater matrix prior to analysis. Seven replicate analyses of the 2.0 $\mu\text{g/L}$ addition of total cyanide (TCN) from a standard mixture were performed in order to evaluate the method detection limit (MDL) as prescribed by the Code of Federal Regulations,²²

$$\text{MDL} = \frac{3.14 \times S \times \text{concn}_{\text{calibrant}}}{\text{height}_{\text{av}}}$$

where S is the standard deviation of the response of the seven replicates. Using these data, the MDL was calculated to be 0.5 $\mu\text{g/L}$ as CN^- . However, the routinely employed practical quantitation limit was 2 $\mu\text{g/L}$, because in practice, the coefficient of variation of replicate analyses below this concentration was often in excess of 25%.

Effect of Different Chemical Species on Total Cyanide Analysis by the Flow Injection Procedure. The Standard Method procedure suggests that various components of wastewater may provide bias in the analytical results for TCN. The major suspects in this group were selected to test for their impact on the measurement of 12 $\mu\text{g/L}$ TCN (as CN) in LGW when present at two levels, 20 and 200 mg/L. In addition to nitrite, nitrate, and aldehydes, four chlorine quenching agents were studied: ascorbic acid; sodium sulfite, sodium thiosulfate, and sodium *m*-arsenite. Table 1 summarizes the results of analysis of the water to which each agent was added in separate containers and then the pH raised to 12. TCN results are shown along with the standard deviation of three replicate analyses. Although acetaldehyde has no impact on the level of cyanide analyzed, formaldehyde does, as a result of its documented conversion of free cyanide to cyanohydrin,³ which is not detected by the analytical system. Free chlorine produces volatile cyanogen chloride, which is probably lost from the sample vessel before analysis and thereby reduces the level of cyanide detected. The presence of nitrate leaves the level of cyanide intact, but nitrite can form nitrous acid during

Table 1. Effect of Different Chemical Species on Total Cyanide Analysis by the Flow Injection Procedure^a

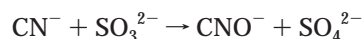
added component	component concn (mg/L)	TCN ($\mu\text{g/L}$)
none	none	12.0 ± 0.5
acetaldehyde	20	12.0 ± 0.9
	200	11.6 ± 0.8
formaldehyde	20	6.3 ± 0.3
	200	4.6 ± 0.2
free chlorine	20	3.9 ± 0.1
	200	4.3 ± 0.1
sulfite	20	4.6 ± 0.2
	200	6.7 ± 0.3
thiosulfate	20	19.1 ± 0.6
	200	85.3 ± 1.4
ascorbic acid	20	9.7 ± 0.4
	200	7.3 ± 0.3
<i>m</i> -arsenite	20	12.0 ± 0.4
	200	12.4 ± 0.4
nitrate	20	12.8 ± 0.4
	200	12.2 ± 0.5
nitrite	20	9.4 ± 0.2
	200	9.4 ± 0.2
sulfide	20	113 ± 5.4 (12.4 ± 0.2)
	200	$26.4 \pm 0.1 \text{ mg/L}$ ($13.4 \pm \mu\text{g/L}$)

^a Values in parentheses for sulfide are the results of analysis after adding lead carbonate and filtering the precipitate.

the analysis, which can engage cyanide in various undocumented reactions. No attempt was made in this set of experiments to remove any of the added components or their resultant reaction products with cyanide prior to analysis.

In the case of sulfide, two sets of experiments were performed. The results in parentheses are those exhibited after adding lead carbonate and filtering the precipitated sulfide. It is clear that without this treatment, such high levels of sulfide will produce the positive bias shown by the levels of "apparent" TCN measured. It is also clear that the bismuth nitrate in the carrier stream has reduced the levels somewhat but is unable to suppress the evolution of H_2S from such elevated levels of sulfide in the water. After this experiment, all wastewaters analyzed in the UNC laboratory were treated for sulfide removal.

In terms of chlorine quenching agent, sulfite converts cyanide to cyanate most likely according to the reaction shown below and is, therefore, an unsuitable quenching agent for residual chlorine in disinfected wastewaters.



We were somewhat surprised at the cyanide loss effected by the presence of ascorbic acid and the large apparent signal increase due to thiosulfate. In the latter case, this can only be attributed to the formation of sulfide during digestion, which is known to be the only major detector interference, as illustrated by the last row of the table. These results suggest the use of ascorbic acid, sodium sulfite, and sodium thiosulfate may not be suitable for the quenching of residual chlorine in effluent samples. Although the two selected concentration levels were somewhat arbitrary and high, they reflect the potential pitfalls of the use of excess amounts of reagents. Among these agents, only sodium *m*-arsenite appears to be a realistic option for quenching residual chlorine

(22) Code of Federal Regulations 40, Part 136, Appendix B; U.S. Government Printing Office: Washington, DC, July 1, 1998.

Table 2. Impact of Quenching Residual Chlorine on Cyanide Stability^a

quenching agent	concn, mg/L	experiment	cyanide concn, $\mu\text{g/L}$
thiosulfate	200	1	548
		2	459
sulfite	141	1	11.8
		2	4.4
ascorbic acid	621	1	12.6
		2	16.1
arsenite	377	1	4.6
		2	20.0

^a Amount of cyanide originally present = 20 $\mu\text{g/L}$.

and was used in all subsequent measurement of TCN in chlorinated wastewaters.

In an attempt to identify the conditions under which the chlorine quenching could be optimized to make use of a quenching agent in the field, we designed two approaches with three different quenching agents, namely, sodium thiosulfate, ascorbic acid, and sodium *m*-arsenite. In the first experiment, 25 mg/L free chlorine was added to a pH 12 solution in LGW containing 20 $\mu\text{g/L}$ total cyanide, the solution was mixed, and within 1 min the quenching agent was added. In the second experiment, the quenching agent was added to the chlorine solution, after which the cyanide was added; the solution was mixed gently; and within 30 s, the pH was adjusted to 12. The results are illustrated in Table 2.

If we use the results of experiment 2 as the basis for cyanide that is not affected by the presence of chlorine, then in experiment 1, the expectation is that the chlorine added to the cyanide would volatilize the latter and remove it from the solution prior to the addition of quenching agent. This is demonstrated for ascorbic acid and sodium arsenite. It can be assumed that the high thiosulfate response was due to the excess agent and its generation of sulfide, which gives a positive bias in the detector. In each case, quenching agents are in great excess and could engage the cyanide in depletion reactions. This could certainly be the explanation for experiment 2 results in which the chlorine is quenched prior to the addition of cyanide. The expectation here is that the cyanide would not be affected by the chlorine and that any lowering of cyanide would be due to interaction with the excess quenching agent. Again, thiosulfate produces a high detector response, whereas sulfite and ascorbic acid produce lower responses, confirming the results of Table 1. Arsenite in experiment 2 shows the least impact. The results of all of these experiments indicate that the random use of chlorine quenching agents cannot be a part of a cyanide analytical procedure, although without knowing in advance the chlorine residual, an excess amount of reagent, but at least in measured amounts, will always have to be used.

The choice of sodium *m*-arsenite as the chlorine quenching agent least likely to impact TCN measurements was verified by analyzing a series of replicate synthetic solutions and spiked effluents, the results of which (the average of duplicate analyses and their difference) are presented in Table 3. After verifying calibration of TCN in LGW, the next group of samples tested the impact of *m*-arsenite on a 0.1 M sodium hydroxide solution made

in LGW, which was spiked with three different concentrations of total cyanide: 5, 10, 50 ppb total cyanide as cyanide ion. The *m*-arsenite was added at three different concentrations (28, 56, and 112 ppm) for each total cyanide concentration. At 28 ppm *m*-arsenite, there is enough capacity to remove the highest typical chlorination doses used at municipal wastewater treatment. The other doses were employed to see the impact of the quenching agent at extreme excess. The resulting total cyanide concentrations were determined and are listed in the table. The spike recovery could then be determined by comparing the total cyanide concentration of the samples that had both cyanide and *m*-arsenite added and the 0.1 M sodium hydroxide solution. These recoveries were within the acceptable range (75–125%) for all but one sample in this group. With this high corroborating evidence, it appears that the *m*-arsenite does not appear to impact the total cyanide concentration for sodium hydroxide solutions made with LGW that are spiked with cyanide.

The next group of experiments tested the impact of *m*-arsenite on wastewater samples. Effluent wastewater samples were collected from treatment plant D2. This plant practices UV irradiation as the disinfection process; consequently, the wastewater was never chlorinated. Samples of wastewater were collected prior to the disinfection process to emulate the condition of the wastewater entering a chlorination process at other plants. Wastewater samples were spiked at three different concentrations of total cyanide (5, 10, and 50 ppb) and quenched with 56 ppm *m*-arsenite. These samples were compared to the wastewater sample to which 56 ppm *m*-arsenite was added but with no added cyanide to evaluate spike recoveries. The recoveries, which were higher than expected, were evaluated by comparison to the wastewater sample at pH > 12 with 56 ppm of *m*-arsenite added. This indicates that the *m*-arsenite did not negatively impact the total cyanide concentrations, as demonstrated by other disinfectant quenching agents. An explanation for the higher than expected recoveries can be partly attributed to the use of the lower of the two values for TCN in effluent (2.84 versus 3.56 $\mu\text{g/L}$). When making the calculations using the latter value, the recovery for 5 $\mu\text{g/L}$ spiked TCN is closer to that obtained for 5 $\mu\text{g/L}$ in 0.1M NaOH. For 50 $\mu\text{g/L}$ spiked TCN in wastewater, the recovery is similar to that for this level and the quenching agent in LGW. The anomaly at 10 $\mu\text{g/L}$ is most likely explained by the poorer precision with that set of data.

The final step examined the effect of chlorination on total cyanide concentration when the residual chlorine was quenched with *m*-arsenite. An aliquot of the effluent wastewater D2 was chlorinated at 25 ppm as Cl_2 and quenched at three different doses of *m*-arsenite (28, 56, and 112 ppm). There were no cyanide spikes in these samples. The impact of the *m*-arsenite could be determined by analyzing the resulting cyanide concentrations and comparing these results to a wastewater sample that was chlorinated at the same dose but not quenched. The resulting cyanide concentrations for these chlorinated wastewaters were 2.6, <2, and <2 $\mu\text{g/L}$, respectively. This indicates that these samples had rather low cyanide concentrations, most of which were below detection. When used on the chlorinated wastewater, the *m*-arsenite did not produce the positive bias associated with other quenching agents.

Table 3. A Summary of the Total Cyanide Concentration (TCN) and the Associated Sample Treatment Procedures

sample treatment	TCN ($\mu\text{g/L}$ as CN^-)	cyanide spike recovery (%)
effluent at ambient pH	<2	NA ^a
25 ppm free chlorine in LGW	<2	NA ^a
25 ppm free chlorine in effluent at $t = 0$	<2	NA ^a
0.1 M NaOH	<2	NA ^a
5 ppb total cyanide in 0.1 M NaOH	6.7 ± 0.8	133
10 ppb total cyanide in 0.1 M NaOH	10.5 ± 0.4	105
50 ppb total cyanide in 0.1 M NaOH	53.2 ± 1.5	106
28 ppm <i>m</i> -arsenite in 0.1 M NaOH	<2	NA ^a
56 ppm <i>m</i> -arsenite in 0.1 M NaOH	<2	NA ^a
5 ppb total cyanide in 0.1 M NaOH with 28 ppm <i>m</i> -arsenite	4.3 ± 0.7	85
5 ppb total cyanide in 0.1 M NaOH with 56 ppm <i>m</i> -arsenite	5.0 ± 0.8	100
5 ppb total cyanide in 0.1 M NaOH with 112 ppm <i>m</i> -arsenite	5.5 ± 0.8	110
10 ppb total cyanide in 0.1 M NaOH with 28 ppm <i>m</i> -arsenite	11.5 ± 0.5	115
10 ppb total cyanide in 0.1 M NaOH with 56 ppm <i>m</i> -arsenite	11.8 ± 0.4	118
10 ppb total cyanide in 0.1 M NaOH with 112 ppm <i>m</i> -arsenite	12.2 ± 0.6	122
50 ppb total cyanide in 0.1 M NaOH with 28 ppm <i>m</i> -arsenite	68.1 ± 2.1	136
50 ppb total cyanide in 0.1 M NaOH with 56 ppm <i>m</i> -arsenite	60.7 ± 1.8	121
50 ppb total cyanide in 0.1 M NaOH with 112 ppm <i>m</i> -arsenite	50.5 ± 0.9	101
effluent with 28 ppm <i>m</i> -arsenite	3.56 ± 0.4	NA ^a
effluent with 56 ppm <i>m</i> -arsenite	2.8 ± 0.6	NA ^a
effluent spiked with 5 ppb total cyanide and 56 ppm <i>m</i> -arsenite	9.8 ± 0.6	139 ^b
effluent spiked with 10 ppb total cyanide and 56 ppm <i>m</i> -arsenite	17.1 ± 3.2	143 ^b
effluent spiked with 50 ppb total cyanide and 56 ppm <i>m</i> -arsenite	64.8 ± 3.1	124 ^b
25 ppm chlorinated effluent quenched with 28 ppm <i>m</i> -arsenite	2.6 ± 0.2	NA ^a
25 ppm chlorinated effluent quenched with 56 ppm <i>m</i> -arsenite	<2	NA ^a
25 ppm chlorinated effluent quenched with 112 ppm <i>m</i> -arsenite	<2	NA ^a

^a Not applicable. ^b Calculated as [(measured TCN - 2.84)/spike level] \times 100.

Comparison of the Two Methodologies. To determine if the inadequacies of the two analytical methods were a direct function of the application to which the method was put, a series of treatment plants that used either UV or chlorination for disinfection were surveyed. Samples were collected at various points throughout the treatment process to determine where a source of apparent cyanide was formed if it was not present at the same levels in the feedwater and effluent from the plant. The first sample collection point was immediately before the point of disinfection; the second point was immediately after disinfection of the wastewater; the third sample was collected at the effluent point of the plant, the point from which samples are collected for monitoring compliance with the effluent cyanide permit. For some plants, this sample point was immediately before the outfall pipe, and at others it was immediately after the point of final disinfection in the plant. Some plants using chlorination follow this with dechlorination before a sample is collected, and others do not dechlorinate.

Total cyanide levels were compared using the automated flow injection procedure and Standard Method on each of these samples, with the Standard Method being applied on split samples in three laboratories. Samples collected at the plants were analyzed as collected and after addition to the pH 12 solutions of spiked levels of free and complexed cyanide, representing a total cyanide spike level of 10 $\mu\text{g/L}$. Samples destined for UNC and lab 2 were treated identically for removal of residual chlorine (56 ppm sodium *m*-arsenite), whereas lab 1 used ascorbic acid. The collected samples were split for interlaboratory analysis at our laboratory (UNC), conducting both methods, and two state-approved laboratories (lab 1 and lab 2) utilizing the Standard Method. Although the UNC laboratory treated all samples for removal of sulfide, labs 1 and 2 did not. The quantitation limits at UNC were 2 $\mu\text{g/L}$ for

both methods and 5 $\mu\text{g/L}$ at labs 1 and 2. The comparative results are shown in Table 4 and reveal a variety of both method discrepancies and anomalies in the plant waters.

Reviewing the results for the plants practicing UV disinfection, none had detectable cyanide in their pre-effluent waters and, following disinfection, there was barely any discernible increase except in the case of the lab 2 analysis of plant F1. Since the spike recovery for this laboratory's sample was in an acceptable range and the coefficient of variation was 5%, one can only surmise that perhaps this water may have undergone a certain degree of denitrification between sampling points that elevated the level of nitrite in the disinfected effluent. With the uncertain predictive outcome of the Standard Method, this could be an example of the nitrite becoming a precursor to cyanide formation during sample processing in this laboratory. The chlorinated waters were, however, a different story. Although the levels of TCN in the prechlorinated water at this plant would barely have made compliance, there is no doubt that either a method interference such as thiocyanate in the Standard Method or the presence of chlorine has contributed to apparent TCN formation. Thiocyanate is a documented interference in the Standard Method but is not detected in the FIA method. This could account for the higher value by the Standard Method compared to FIA. Nevertheless, the high levels of TCN in this plant's water are more likely the results of a chlorine interaction generating cyanide and measured by both methods. Moreover, the Standard Method shows inappropriate spike recovery. At UNC, our calibration curves were adjusted to account for these elevated levels, whereas it is likely that lab 2 may have been analyzing this sample outside its linear range to have obtained such a different result from those produced from the university laboratory.

Table 4. Total Cyanide Analysis of Various Wastewaters, Pre- and Postdisinfection, Using Flow Injection UV Digestion (FIA) and Acid Digestion Complexation (SM)

utility/plant	pre-effluent		pre-effluent with spike ^a		effluent				effluent with spike				posteffluent		posteffluent with spike	
					UNC		lab 1	lab 2	UNC		lab 1	lab 2	UNC	UNC	UNC	UNC
	SM ^b	FIA ^c	SM	FIA	SM	FIA	SM	FIA	SM	FIA	SM ^d	FIA ^d	SM ^d	FIA ^d	SM ^d	FIA ^d
A1	<2	4.4	12.4	9.4	5	21.4	7	20	11.3	28.3	NA	20	NA	NA	NA	NA
A2	<2	<2	6.4	7.4	7.7	15.7	9	10	11.2	22.7	NA	20	NA	NA	NA	NA
B1	2.1	<2	9.1	8.4	2.9	6.1	<5	10	15.4	38.2	15	20	NA	NA	NA	NA
C1	10.6	9.8	31	16.2	291	212	NA	140	341	226	NA	160	245	169	290	176
C2	<2	4.5	4.7	16.1	6.8	7.8	NA	12	12.1	18.7	NA	18	5.4	15.2	12.3	26.8
D1 ^e	<2	<2	8.9	11.5	<2	2.6	<5	NA	12.1	13.1	NA	NA	NA	NA	NA	NA
D2 ^e	<2	<2	9.5	12.1	<2	<2	<5	<5	13.8	14.7	10	20	NA	NA	NA	NA
E1 ^e	<2	<2	7.4	10.8	<2	2.4	<4	5	11.6	12.3	10	14	NA	NA	NA	NA
F1 ^e	<2	<2	8.1	10.4	<2	2.3	<5	8	14.7	12.4	12	20	NA	NA	NA	NA
H1	<2	4.1	11	10.5	<2	6.2	<2	<5	6.1	14.6	7.8	6	NA	NA	NA	NA
H4 ^e	<2	<2	7.9	11.1	2.1	2.4	<2	<5	11.1	12.5	7.8	5	NA	NA	NA	NA
H5 ^e	<2	<2	8.8	10.9	<2	2.3	<2	<5	4.7	13.3	8	6	NA	NA	NA	NA

^a Spike levels were 10 µg/L TCN except for A1 and A2, which used 5 µg/L. ^b Standard Method for analysis of TCN. ^c Flow injection analysis. ^d NA, sample not analyzed. ^e Plant uses UV for disinfection.

Considering the results of analysis of the samples collected before disinfection, all of which were analyzed only at the UNC laboratories, it appears, on the basis of the near-perfect spike recovery for the flow injection procedure, that the 4.38 (±0.3) µg/L TCN is a true measure in plant A1. Similar acceptable recoveries were obtained by flow injection for plants C1 and C2, suggesting that these prechlorinated waters may well have contained TCN. All other plants appear to have nondetectable TCN in their predisinfected wastewaters.

In the case of plant H1, the poor recoveries by use of the Standard Method in each of the three laboratories points to greater reliability in the FIA generated results, which reflects the general trend observed with chlorinated waters, namely, that regardless of background TCN levels, prior to chlorination, a certain amount of cyanide is being formed during wastewater treatment. Drawing on the case of plant C2, where a sample was also collected after dechlorination (post effluent), it does not appear to be the presence of chlorine by itself that is responsible for the formation, but most likely the interaction between chlorine and components of the wastewater. The discrepancies between the two methods and among the practices of each of the laboratories employing the Standard Method are evident in a review of the disinfected effluents. For all but two plants (E1 and H5, both of which practice UV disinfection), there is no consistency between the analysis of the split samples. At plant A1, both methods practiced at UNC provided acceptable spike recoveries, yet the levels of TCN measured vary widely. Moreover, the results from labs 1 and 2 for plant A1 are not consistent. Lab 2 showed no spike recovery. There is no single example of a plant for which the spike recoveries in the same matrix but analyzed by different laboratories or methods are in the same range. However, there is some good correlation between the two methods used at UNC on all pre-effluent samples, except those from utility C. Correlations between the two methods are also good in effluent samples from plants D2 and E1. It should be noted that at UNC, triplicate analyses by FIA were more precise (coefficient of variation = 5–7%) than by the standard method (8–12%). Laboratories 1 and 2 provided only the results of duplicate sample

analysis whose relative percent difference was in the range 10–20%.

For the UV plants, the data generated by the two methods for the same sample were practically identical. The exception would be for the spiked effluent in plant H5 by the Standard Method, but this is, indeed, an anomaly. It is, however, the disparity between the results of analysis of the same sample using the Standard Method in the three laboratories that more than anything highlights the inadequacy of the indirect acid distillation approach to TCN analysis.

CONCLUSIONS

The wide variation between the results from different laboratories using the same indirect Standard Method of acid distillation and complexation is an indication of the impact of not standardizing sample handling, processing, and analytical techniques. Indeed, most of the utilities involved in this study now recognize this, even though they might not have the resources to fully implement all aspects of the suggested protocols in the future, and this is in no small measure due to the method's awkwardness and hazardous nature.

The FIA procedure presented in this paper provides for rapid turnaround on analysis of TCN, protects the operator from exposure to hazardous chemicals, including HCN, and has been proven to generate precision reproducibility on the analysis of UV disinfected and chlorinated wastewaters from municipal wastewater treatment plants. In particular, because the manual Standard Method is subject to so many sample-handling procedures, it can generate different analytical results for the same sample analyzed in different laboratories. As a closed and complete system, the FIA direct analysis procedure will not be impacted by the different practices of personnel and is more likely to be reproducible in interlaboratory measurements. With the use of sodium *m*-arsenite as a chlorine quenching agent and precipitation/filtration of sulfide, the FIA method provides major improvements over the traditional methods for TCN analysis. The results of this study also demonstrate the likelihood that permit violations may occur as a result of cyanide generation during wastewater

treatment. The latter issue will be much easier to explore and identify with the use of FIA.

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