ROBUST CYANIDE ANALYSIS IS FUNDAMENTAL FOR SAFE DRINKING WATER

Several regulatory bodies have set guidelines for cyanide levels in drinking water to ensure its quality and to protect consumers. Traditionally, cyanide measurement in drinking water involves colorimetric and spectrophotometric methods, but these suffer the drawbacks of requiring a distillation step and are subject to a range of interferences. Alternative approaches are needed to achieve the measurement sensitivity and robustness required today. Ion chromatography with pulsed amperometric detection (IC-PAD) is proving highly effective in this application.

Introduction

Cyanide is well-known as a highly toxic substance. It is present naturally in a variety of foods, including cassava, bamboo shoots and some fruit pits, and is also generated by microorganisms. Industrially, cyanide is used in many processes, including plating and mining, and it may be released into the environment from burning coal and plastics. In the US, drinking water contamination with cyanide typically originates from an industrial source or is the result of leaching from waste sites.

The US government classifies cyanide as a regulated inorganic contaminant in drinking water. This is set out in US National Primary Drinking Water Regulations, 40CFR 141.62, and enforced by the US Environmental Protection Agency (EPA) and state EPA agencies. Since bottled water is classified as a food, the US Food and Drugs Administration (FDA) Center for Food Safety and Applied Nutrition (CFSAN) is responsible for its regulation. The maximum contaminant level (MCL) for drinking water is 200 µg/L cyanide, as free cyanide, although levels found are typically much lower.

Table 1: Cyanide waveform and experimental conditions

Time (sec)	Potential vs Ag/AgCl (V)	Gain region	Integration	Ramp
0.00	-0.10	Off	Off	On
0.20	-0.10	On	On (start)	On
0.90	-0.10	On	Off (end)	On
0.91	-1.00	On	Off	On
0.93	-0.30	On	Off	On
1.00	-0.30	On	Off	On

Conditions	
Columns	Thermo Scientific™ Dionex™ IonPac™ AS15 Analytical, 2 x 250 mm (P/N 053941) Dionex IonPac AG15 Guard, 2 x 50 mm (P/N 053943)
Flow Rate:	0.25 mL/min
Eluent:	63 mM Sodium hydroxide (31.5% Eluent B, 200 mM sodium hydroxide)
Column Temp.:	30 ºC
Tray Temp.:	10 ºC
Inj. Volume:	10 µL (PEEK sample loop, P/N 042949), full loop injection
Detection	Pulsed Amperometric Detection (PAD)
Waveform	See Table 1
Electrodes:	Reference: pH-Ag/AgCl electrode (P/N 061879) in AgCl mode
Working	Certified Disposable Ag Working Electrode
Background:	3-13 nC versus Ag/AgCl
Pressure:	~1100 psi
Noise:	< 7 pC
Run Time:	25 min
Syringe speed:	4
Flush Volume:	250 µL

Measurement Approaches and Their Limitations

Cyanide can be determined as total cyanide, dissociated cyanide, or free cyanide. Regulatory levels refer to free cyanide which poses the greatest health concern because of its bioavailability and toxicity.

EPA-approved methods for determining free cyanide involve spectrophotometry, colorimetry, or ion-selective electrode detection. Many current methods have inherent drawbacks. The colorimetric and spectrophotometric methods require a distillation step, and they suffer from several interfering factors. These include difficulties with the high pH solutions used to stabilize water samples, the presence of oxidizers and of sulfur-bearing compounds. The ion-selective electrode method does not require distillation but is highly matrix sensitive.

Ion chromatography (IC) methods for cyanide use either direct current (DC) amperometric detection or pulsed amperometric detection (PAD). No distillations are needed, and there is little or no problem with the interfering substances listed above. The DC method does, however, exhibit electrode fouling over time, whereas the IC-PAD method overcomes all these issues.

Evaluating IC-PAD to Determine Free Cyanide Levels in Drinking Water

Free cyanide analysis of water samples was carried out using an IC system (Thermo Scientific Dionex ICS-3000, similar to the current ICS-6000) equipped with columns specific for the analysis of trace anions in high-purity water matrices (Thermo Scientific Dionex IonPac AS15 and AG15 columns) and an electrochemical detector (Thermo Scientific Dionex ICS-3000 ED or ICS-6000 ED) with an amperometric cell containing working, reference, and counter electrodes. This application uses a disposable silver working electrode.

Pulsed amperometric detection involves the brief application of a potential across the working and reference electrodes, followed by higher or lower potentials to clean the working electrode. This avoids the fouling and loss of signal that can occur in DC amperometry. The series of applied potentials is referred to as a waveform. Repeated application of a waveform is the basis of pulsed amperometry. PAD provides a stable and fresh working electrode surface every cycle of the waveform (1 second). For this study, the waveform was optimized for cyanide but can also detect sulfide, bromide, and thiosulfate. Table 1 shows the waveform and summarizes the measurement conditions used.

Drinking water samples were taken from the City of Sunnyvale, City of San Jose and Twain Harte Valley, CA. The sources of Twain Harte Valley (an old gold mining region) drinking water and Alamitos Creek in Almaden region (old mercury mining) of San Jose, were selected because of their mining history and potential presence of free cyanide. Since cyanide is reactive and unstable, with oxidizing agents causing decomposition and any free cyanide present at neutral pH volatilizing to hydrogen cyanide, samples were stabilized as soon as practicable by treatment with sodium hydroxide solution.

Further details of the experimental setup, eluent, standards and sample preparation are provided in reference 1.

Results

Investigating Potential Interfering Factors

EPA methods cite sulfide and sulfide-generating compounds as potential interferences because sulfide complexes with free cyanide to form thiocyanate. Nitrate, nitrite, and chlorine are also interfering substances, while copper, iron, and

Anion[3]	Recovery
None	102.9 ± 2.3%
Bromide	99.9 ± 2.6%
Iodide	99.9 ± 2.9%
Sulfide	95.9 ± 1.7%
Sulfite	97.7 ± 2.5%
Thiocyanate	110.1 ± 2.6%
Thiosulfate	99.9 ± 2.7%

Table 2: Effect of bromide, iodide, sulfide, sulfite, thiocyanate, and thiosulfate on cyanide recovery.

other transition metals complex with free cyanide, making it unavailable for measurement. In the IC-PAD study reported here, the electroactive ions iodide, thiosulfate, bromide, thiocyanate, and sulfide are all potential interferences as they are detected using the silver working electrode and cyanide optimized waveform.

The interference effects of non-oxidized and partially oxidized sulfur-containing anions, bromide, and iodide were examined by analyzing solutions of 10 µg/L cyanide and 20 µg/L of each potential interfering anion. Table 2 shows that the resulting free cyanide concentrations were not significantly affected by any of the anions. There was a small decrease with sulfide and a small increase with thiocyanate, but neither is expected in high concentrations in drinking water since sulfide is normally removed during sanitation. These experiments confirm that the cyanide waveform detects thiosulfate, sulfide and bromide under the conditions used, but does not detect sulfate, thiocyanate, or iodide. Where it is necessary to resolve cyanide from sulfide, a different set of chromatography columns (Thermo Scientific Dionex IonPac AS7) is recommended.

Investigation of the effects of dissolved iron, copper and nickel on free cyanide determinations involved treating a 10 µg/L cyanide standard with each metal. The use of a 600 µg/L solution of iron reflects expected levels in drinking water, while copper and nickel concentrations were arbitrarily set at 300 µg/L. Further testing included treating the metal solutions with proprietary sample preparation cartridges for matrix clean up (Thermo Scientific Dionex OnGuard II H) before adding them to cyanide standards. In the iron solution, the free cyanide concentration loss was comparable to that of the untreated cyanide control over 3 days (Figure 1) whereas after 92 h only 28% of the free cyanide remained in the copper solution (Figure 2), and in the

Table 3: Recovery of cyanide in treated water samples (Dionex OnGuard II H Cartridges)

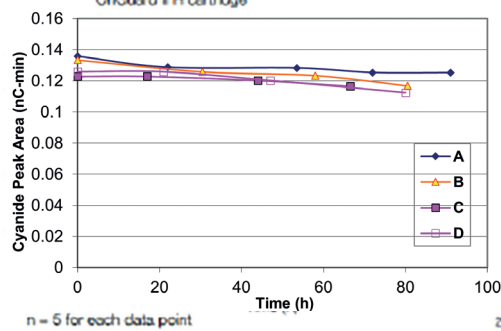| Concentration of cyanide spike (µg/L)	City of Sunnyvale drinking water	City of San Jose drinking water	Twain Harte Valley drinking water	Twain Harte Valley Flume
5	80.6 ± 5.5%	87.3 ± 6.4%	95.9 ± 2.5%	81.1 ± 3.2%
10	99.5 ± 2.8%	99.4 ± 2.5%	96.8 ± 3.1%	93.1 ± 1.5%

Figure 1: Effect of dissolved iron on free cyanide (10 µg/L)

nickel solution free cyanide decreased to 75% within 20 h then stabilized for the remainder of the 3-day experiment (Figure 3).

Figures 1, 2 and 3 also show results that indicate the effective removal of metals from each solution using the sample pre-treatment (graph B). In addition, they show that free cyanide concentration declines in all samples over 3 days, so measurements should be made as quickly as possible.

Method Qualification

The IC-PAD cyanide method was qualified before testing real drinking water samples by determining: linearity over a 50-fold concentration range, typical noise, method detection limit (MDL), reproducibility and ruggedness. Linearity, ascertained by testing six replicates of six standards, was good (r^2>0.999) over the concentration range 2.0 to 100 µg/L. For each of five disposable electrodes, noise was determined over two 60 min runs, when no sample was injected, measuring the noise in 1 min intervals from 5 to 60 min. This gave a noise value of 7.0+/-1 pC (n=10). MDL was defined as the peak within a standard that has a height three times that of the noise level, and for this application was 1.0 µg/L. Signal to noise ratio of a 2.0 µg/L cyanide standard was 16.3 +/-4.8 (n=10).

Reproducibility and ruggedness were determined over 140 injections, approximately 62 h. Figures 4 and 5 show the results, indicating that retention times and peak areas remained stable throughout. Retention time and peak area reproducibility was 5.78 +/- 0.027 min and 0.1232 +/- 0.0016 nC-min respectively.
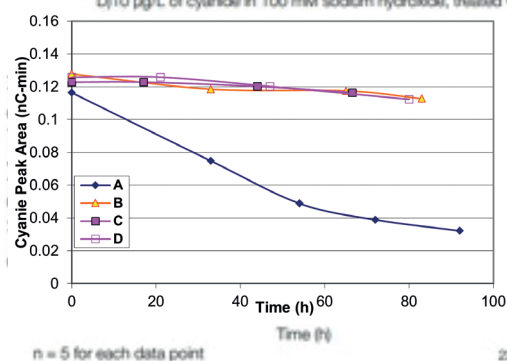

Figure 2: Effect of dissolved copper on free cyanide (10 µg/L)

Cyanide Determination in Drinking Water and Surface Water

Free cyanide can be determined in drinking water by IC-PAD. The method shows good sensitivity (MDL of 1 µg/L) and good recovery, and exhibits linearity from 2 to 100 µg/L. Since IC-PAD uses eluents that have a basic pH, this method is compatible with the high pH (pH 13) of total cyanide distillation samples. Unlike other cyanide measurement methods, there is no need

to dilute or neutralize the high pH distillation samples prior to analysis. This has the advantage of retaining the low 1.0 µg/L detection limits.

Drinking water characteristics are subject to seasonal changes. Free cyanide concentrations and spike recoveries of 5 and 10 µg/L cyanide were determined using the IC-PAD method for the City of Sunnyvale water throughout the study and some changes were observed. During the summer, there was good spike recovery, including with the addition of sulfide. No free cyanide was measured in the unspiked samples.

The same analysis method was used to measure free cyanide and cyanide recovery from two drinking waters sampled in the fall (City of San Jose and City of Sunnyvale) and one surface water sample (Alamitos Creek). Results showed no initial concentrations of free cyanide and variable recovery of cyanide spikes, with City of Sunnyvale results contradicting those from the summer. It is therefore possible that the City of Sunnyvale water had changed since the initial sampling.

Cyanide recovery from City of San Jose over time showed a similar trend to that observed with metal interferences. As a consequence, all samples were treated with the OnGuard II cartridges and the recovery experiments were repeated. Drinking and surface water samples were also analyzed from the Twain Harte Valley in the same way. The results (Table 3) show good recovery from all the treated samples and Figure 6 (City of Sunnyvale drinking water) exemplifies results with and without the spike. There was also good stability (>84% of the initial peak response) for 31 h (results not shown). No free cyanide was measured in any of the drinking water or surface water samples.

Disposable Silver Working Electrode Performance

The lifetimes of five disposable silver working electrodes were evaluated during the interference experiments, method qualification and municipal drinking water testing. Each electrode was installed, tested and removed after two weeks of continuous use. Average peak areas of 10 µg/L cyanide in 100 mM sodium

Figure 3: Effect of dissolved nickel on free cyanide (10 µg/L)
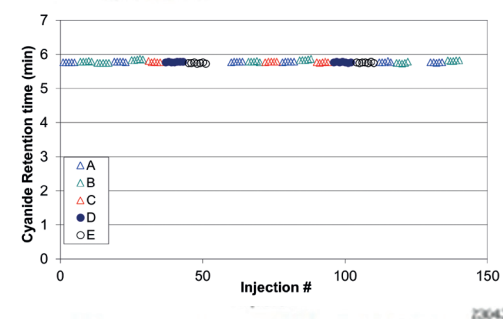
Figure 4: Retention time stability of 10 µg/L cyanide

Figure 5: Peak area stability of 10 µg/L cyanide

hydroxide across the five electrodes showed less than 1% variation. All five exceeded the 14-day lifetime specification.

Sensitive Robust Cyanide Analysis

Ensuring cyanide levels in drinking water remain within acceptable limits is critical to human health. However, current spectrophotometric and colorimetric analytical methods require a cumbersome distillation step and are prone to a range of interferences, while ion-selective electrode techniques exhibit considerable matrix sensitivity. IC-PAD offers an alternative analytical approach with good sensitivity, recovery, and linearity, as the evaluation presented above shows. Since cyanide levels in drinking water are generally expected to be very low or absent, this work also highlights the importance of including spike samples of the waters being tested, as a check on analytical accuracy.

The IC-PAD method has the advantage of being able to tolerate the basic pH conditions needed to stabilize water samples for cyanide determination. As part of the workflow, it is easy to remove potentially interfering dissolved transition metals using sample pre-treatment cartridges. Overall, IC-PAD analysis delivers fast, accurate free cyanide measurements, is compatible with the basic solutions used to preserve water samples and is unaffected by other compounds typically found in drinking water. It, therefore, provides laboratories with a sensitive, robust and higher throughput alternative to spectrophotometric, colorimetric, and ion-selective electrode techniques, supporting enhanced testing capability and productivity.
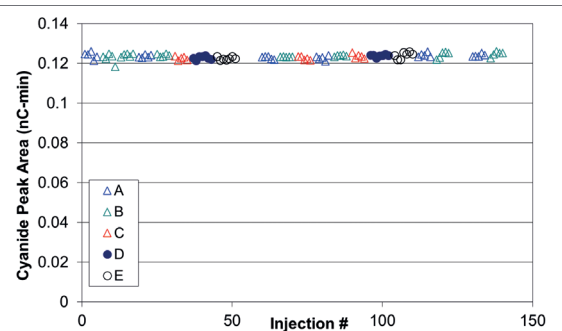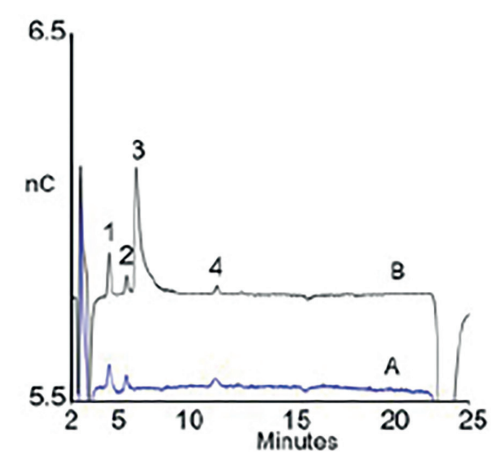

Column: IonPac AS15 and guard, 2-mm
Eluent: 63 mM Sodium hydroxide (31% Eluent B, 200 mM sodium hydroxide)
Column Temp: 30 °C
Tray Temp.: 10 °C
Flow rate: 0.25 mL/min
Inj. Volume: 10 µL
Detection: PAD, Cyanide waveform
Peaks:
1. Unknown
2. Chloride
3. Cyanide, 10 µg/L
4. Bromide

Figure 6: Treated City of Sunnyvale drinking water A) without, and B) with 10 µg/L cyanide

References

1. Christison, T. & Rohrer, J. Direct determination of cyanide in drinking water by ion chromatography with pulsed amperometric detection. Application Note. 2021. https://appslab.thermofisher.com/App/1679/direct-determination-cyanide
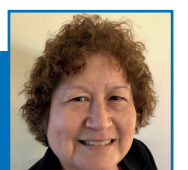
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