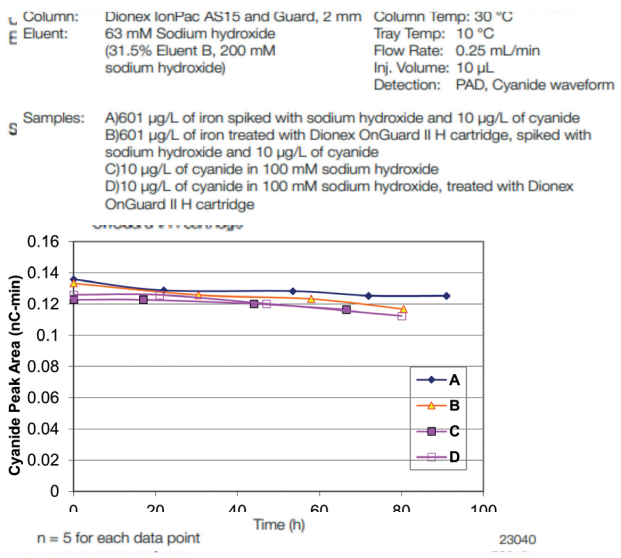


Figure 1: Effect of dissolved iron on free cyanide (10 µg/L)

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.

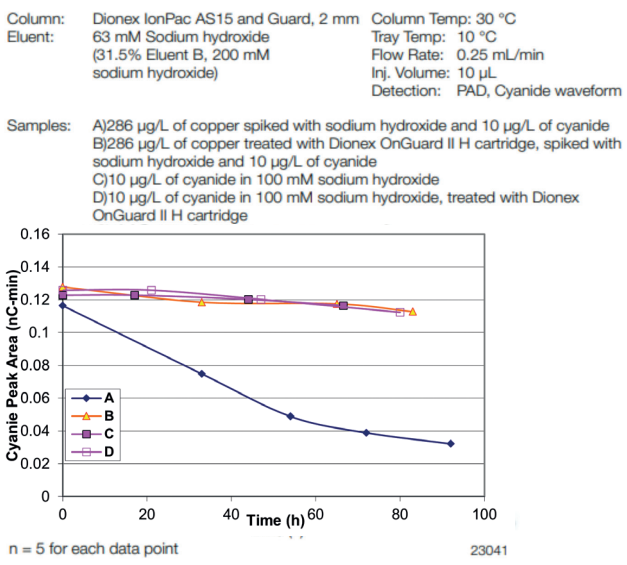


Figure 2: Effect of dissolved copper on free cyanide (10 µg/L)

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

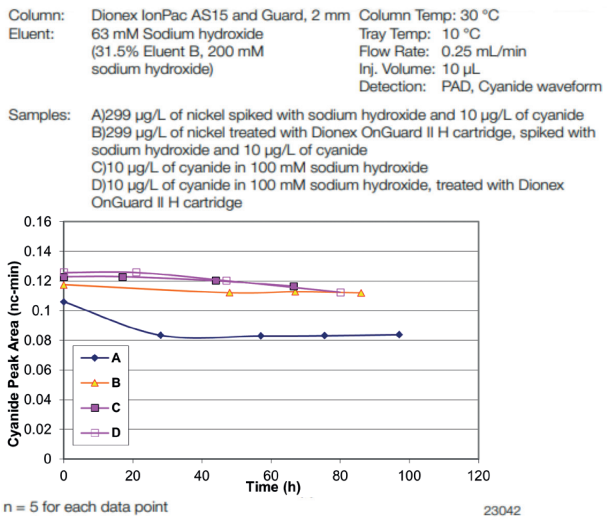


Figure 3: Effect of dissolved nickel on free cyanide (10 µg/L)

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

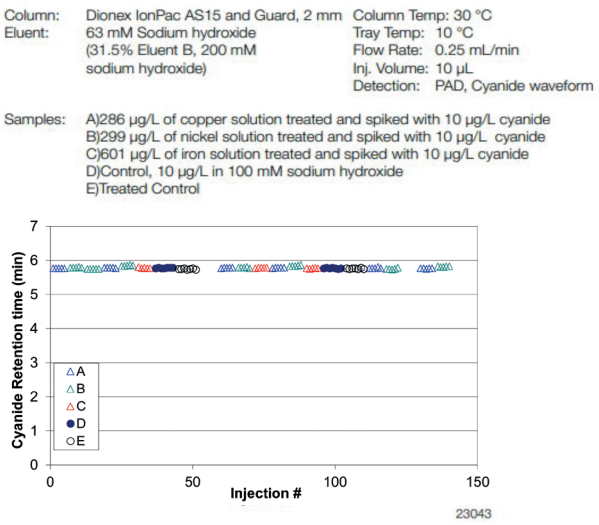


Figure 4: Retention time stability of 10 µg/L cyanide

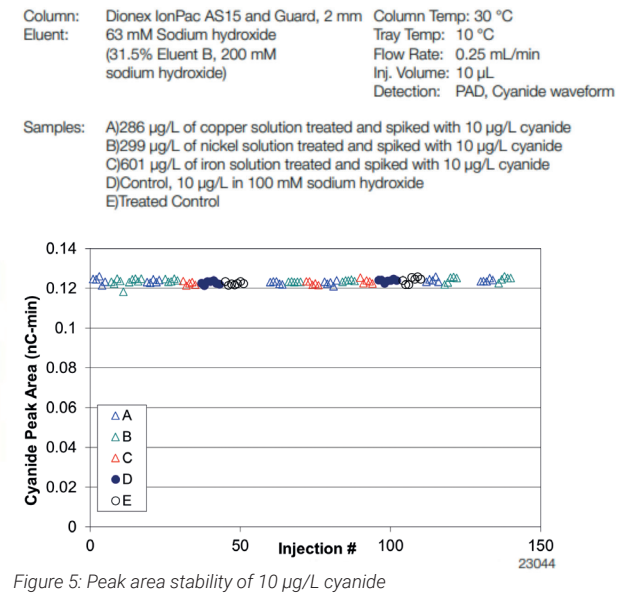


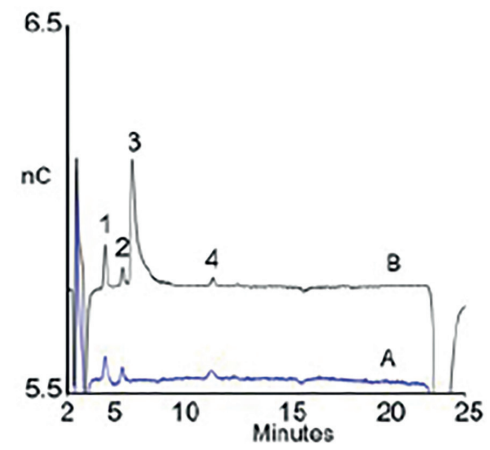
Figure 5: Peak area stability of 10 µg/L cyanide

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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