

# Direct Determination of Cyanide in Drinking Water by Ion Chromatography with Pulsed Amperometric Detection

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## INTRODUCTION

Cyanide is a regulated inorganic contaminant in drinking and bottled water in the U.S., enforced by the U.S. EPA and the U.S. FDA Center for Food Safety and Applied Nutrition (CFSAN), respectively. The typical sources of cyanide in the U.S. are from industrial contamination. In some countries, staple food products such as sorghum and cassava, are also sources of cyanide. This poster discusses the development of an ion chromatography (IC) method with pulsed amperometric detection (PAD) to directly determine free cyanide in drinking water. Drinking water samples are pretreated with a sodium hydroxide solution to stabilize cyanide and then with a cation exchange cartridge to remove dissolved transition metals. Samples are analyzed within three days of sampling. Cyanide is separated from other ions using a high-performance anion-exchange column and detected with a three-potential PAD waveform optimized for cyanide and a disposable silver working electrode. This method demonstrates good retention time stability with <1% RSD (140 injections), linear calibration from 2 µg/L to 100 µg/L cyanide ( $r^2 > 0.999$ ), and a MDL, measured at three times the noise, of 1.0 µg/L. The recovery of spiked cyanide in three drinking water samples and two surface water samples is good, >80%. The electrode-to-electrode reproducibility was ~ 1% RSD of the peak area.

## Cyanide Toxicity

- Disrupts the electron transport chain in the mitochondria membrane and prevents respiration.
- Interferes with iodine uptake by the thyroid.
- Chronic exposure: goiters, some neuron-muscular diseases, and cretinism

## Sources

- Foods: cassava, flax, sorghum, bamboo shoots, and bitter almonds<sup>1</sup>
- Micro-organisms: fungi, algae, and bacteria<sup>2</sup>
- Industrial: plating and mining, and burning coal and plastics

## Regulated Contaminant 40CFR 141.62<sup>3</sup>

- U.S. EPA and state EPA agencies.
- Bottled water by the FDA, Center for Food Safety and Applied Nutrition (CFSAN) division.
- The maximum contaminant level (MCL) is 200 µg/L cyanide, as free cyanide.
- Typical concentrations in U.S. drinking water are from undetected to 10 µg/L.
- In a 1978 U.S. EPA survey, 7% of the drinking water samples had measurable concentrations of cyanide but below the MCL.<sup>4</sup>

## Test Methods

- Total cyanide (EPA 335.2)<sup>5</sup>
  - Distillation with acid and an oxidizing agent
  - Captured in a pH 13 sodium hydroxide solution
  - Determined by colorimetric or titration methods
- The EPA approved free cyanide methods
  - Spectrophotometry (335.1)<sup>5</sup>
  - Colorimetry (335.3) detection<sup>5</sup>
  - Ion selective electrode (ASTM 9213)<sup>6</sup>
- IC Methods
  - DC amperometry detection<sup>7</sup>
  - PAD<sup>8-9</sup>
- Interferences
  - Colorimetric and spectrophotometric methods: Difficulty with high pH solutions, oxidizers, and sulfur-bearing compounds.
  - Ion selective electrode: matrix sensitive.
  - DC amperometry: electrode fouling over time.

This poster describes fast, accurate determinations of free cyanide in drinking water samples, using an anion exchange separation and PAD. The PAD uses a waveform optimized for cyanide detection on a disposable silver working electrode.

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## EXPERIMENTAL

### Equipment

Dionex® ICS-3000 ion chromatography system consisting of:

- Single Gradient (SP) pump module with degas option and gradient mixer
- Detector and Chromatography Module (DC)
- Electrochemical Detector (ED) with an electrochemical cell containing a combination pH-Ag/AgCl reference electrode and a Certified Disposable Silver (Ag) working electrode (Package of 6 electrodes, P/N 063003)
- AS Autosampler with Sample Tray Temperature Controlling option, 1.5 mL sample tray, and 1.5-mL polypropylene sample vials
- Chromeleon® Chromatography Workstation with Chromeleon 6.8

Dionex OnGuard® II H Cartridges (2.5 cc package of 48, P/N 057086)

### Reagents and Standards

- Deionized water, Type 1 reagent-grade, 18 M $\Omega$ -cm resistivity or better, freshly degassed by vacuum filtration
- ACS reagent grade chemicals
  - Sodium cyanide, anhydrous (Aldrich, P/N 20,522-2)
  - Sodium hydroxide, 50% (w/w) (Fisher Chemicals, P/N SS254-500)
  - Copper, nickel, and iron reference standards, certified 1000 ppm  $\pm$  1% (Fisher Chemical), for metal interference experiments
  - Anhydrous sodium bromide, sodium iodide, sodium sulfite, and sodium thiocyanate, nonahydrate sodium sulfide, and pentahydrate sodium thiosulfate, (Aldrich) for interference experiments

### Samples

- Drinking water
  - City of Sunnyvale, CA (sampled on multiple days)
  - City of San Jose, CA
  - Twain Harte Valley, CA
- Surface water
  - Twain Harte Valley, CA (an old gold mining region)
  - Alamos Creek in Almaden region (an old mercury mining region) of San Jose, CA

### Conditions

Columns:	IonPac® AG15, AS15, 2 $\times$ 250 mm
Flow Rate:	0.25 mL/min
Eluent:	63 mM Sodium hydroxide (31.5% Eluent B, 200 mM sodium hydroxide)
Column Temperature:	30 °C
Tray Temperature:	10 °C
Inj. Volume:	10 $\mu$ L, full loop injection
Detection:	PAD
Waveform:	See Table 1.
Reference electrode:	pH-Ag/AgCl electrode (P/N 061879) in AgCl mode
Working electrode:	Certified Disposable Ag Working Electrode
Typical background:	3-13 nC versus Ag/AgCl <sup>a</sup>
System backpressure:	~1100 psi
Noise:	<7 pC
Run time:	25 min

<sup>a</sup> The disposable silver electrodes have a background specification of -45 to + 55 nC versus Ag/AgCl with the recommended waveform.

### Preparation of Standards and Eluent

The sodium hydroxide solutions were prepared with low carbonate, high purity Fisher (Hampton, NH, USA) 50% sodium hydroxide solution.

Freshly degassed, deionized water, Type 1 reagent-grade, 18.2 M $\Omega$ -cm resistivity from a LabConco (Kansas City, MO, USA) water deionization system was used to prepare diluent and eluents.

All of the cyanide standard solutions were prepared in 100 mM sodium hydroxide solution. Use only plastic pipettes, vials, and bottles for this application. Sodium hydroxide will etch glass and the subsequent contaminants will foul the silver working electrode.

We prepared the sulfide stock standards from a recently unopened Aldrich (St. Louis, Mo, USA) bottle because sodium sulfide is hygroscopic and readily degrades. The intermediate and stock sulfide solutions were prepared every two weeks. The working standards were prepared daily.

### Preparation of Samples

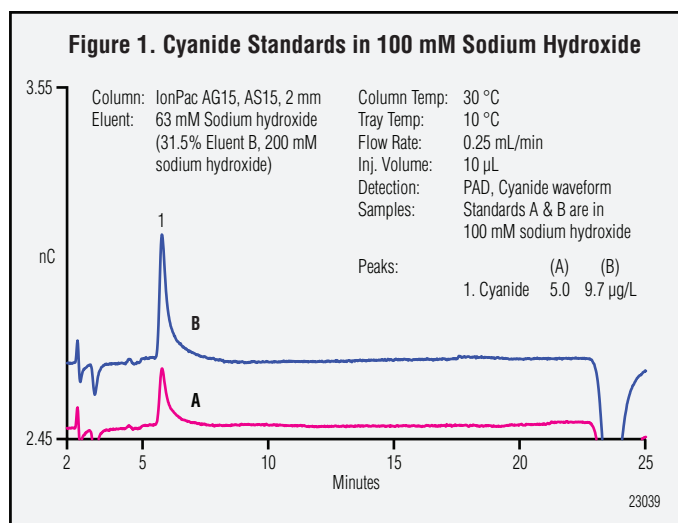
We stabilized the drinking and surface water samples as soon as practical with sodium hydroxide. Sunnyvale and San Jose municipal drinking water samples were stabilized within an hour of sampling by addition of 2.0 g of 50% (w/w) sodium hydroxide solution per 250 g of drinking water. Samples located farther away from the laboratory were collected in 250-mL bottles containing 2 g of 50% sodium hydroxide. The cyanide in these samples is stable for about 3 days.

## RESULTS AND DISCUSSION

Cyanide and other target analytes were separated on a Dionex IonPac AS15 (2 × 250 mm) analytical and guard (2 × 50 mm) columns with 63 mM sodium hydroxide at a flow rate of 0.25 mL/min and 30 °C for 25 min. The analytes were detected by PAD using a disposable silver working electrode, and a three-potential waveform for cyanide (Table 1). The waveform is optimized for cyanide but it can also detect sulfide, bromide, and thiosulfate.

Table 1. Cyanide Waveform				
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	Off	Off	On
1.00	-0.30	Off	Off	On

Figure 1 shows the chromatograms of 5 and 10 µg/L cyanide standards in 100 mM sodium hydroxide using the described separation and detection methods.

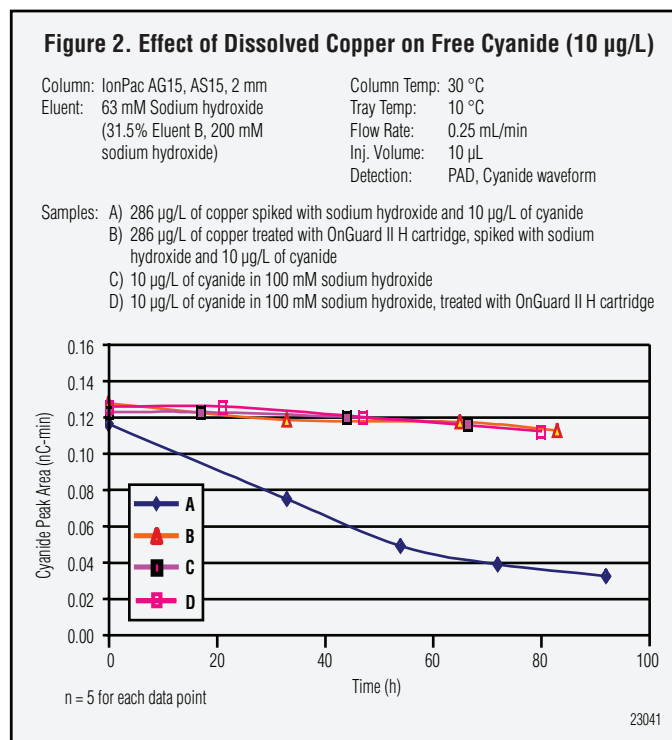


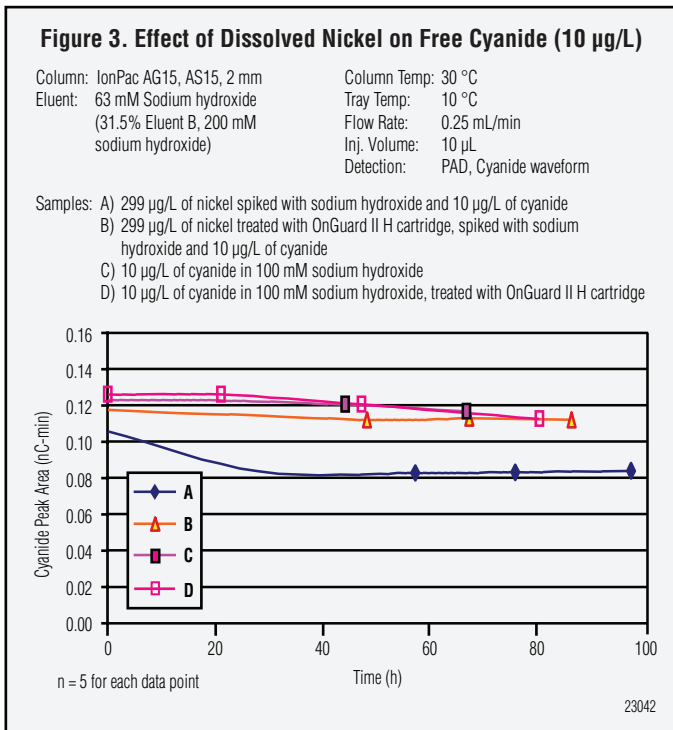
In Table 2, we show good recovery of 10 µg/L of cyanide in presence of 20 µg/L of bromide, iodide, sulfide, sulfite, thiocyanate, and thiosulfate interfering anions.

Anion <sup>a</sup>	Recovery of 10 µg/L Cyanide
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%

n = 10 for each experiment  
<sup>a</sup>The concentration of each anion was 20 µg/L

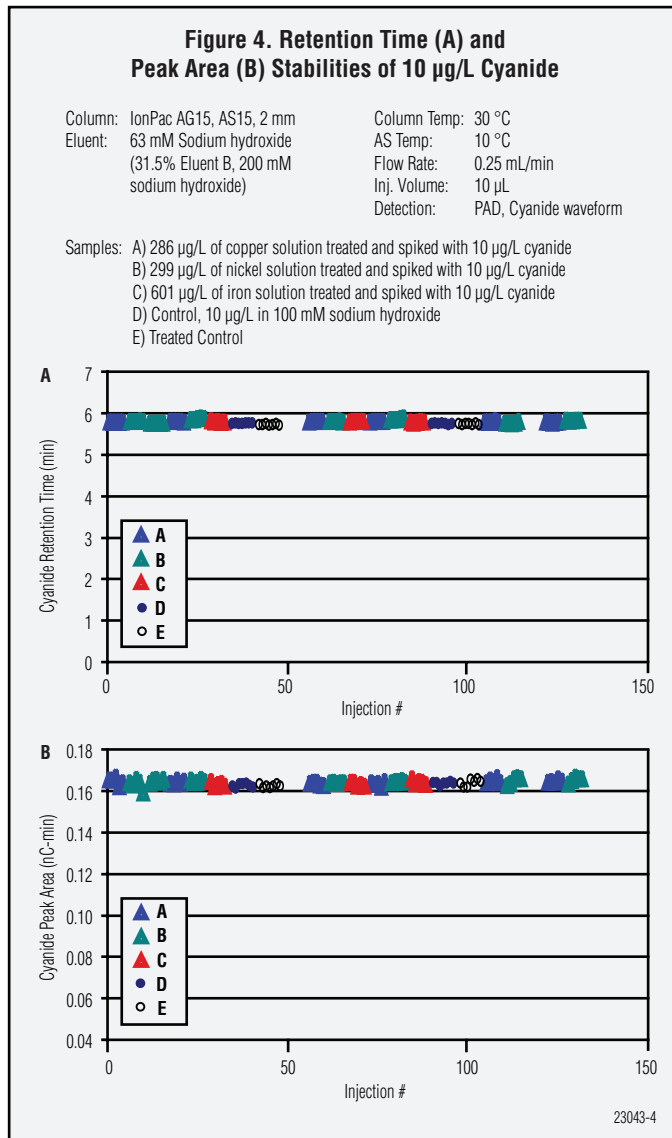
In Figures 2–3 we show the effect of dissolved metals on the determination of free cyanide concentrations. We prepared individual solutions of copper, nickel, and iron (286 µg/L, 299 µg/L, and 601 µg/L, respectively). We treated a portion of the solutions with Dionex OnGuard II H cartridges to remove the dissolved metals. 100 mM sodium hydroxide and 10 µg/L cyanide were spiked into the treated and untreated metal solutions. In the presence of nickel and copper (Figures 2–3), the free cyanide concentrations decreased 30–40% within 28 h. The free cyanide concentration in the untreated iron solution, treated iron solution, and the cyanide controls decreased slightly over 72 h (not shown).





The response of the cyanide peak area to concentration is linear from 2.0 to 100 µg/L,  $r^2 > 0.999$  ( $n=10$ ). For each five disposable electrodes, we determined the noise over two 60-min runs, when no sample was injected, by measuring the noise in 1-min intervals from 5 to 60 min,  $7.0 \pm 1.8$  pC ( $n=10$ ). The noise was similar for five disposable silver working electrodes. We defined the method detection limit (MDL) as the standard with the peak height that is three times the noise level, 1.0 µg/L. The signal to noise of the 2.0 µg/L cyanide standard was  $16.3 \pm 4.8$  ( $n=10$ ).

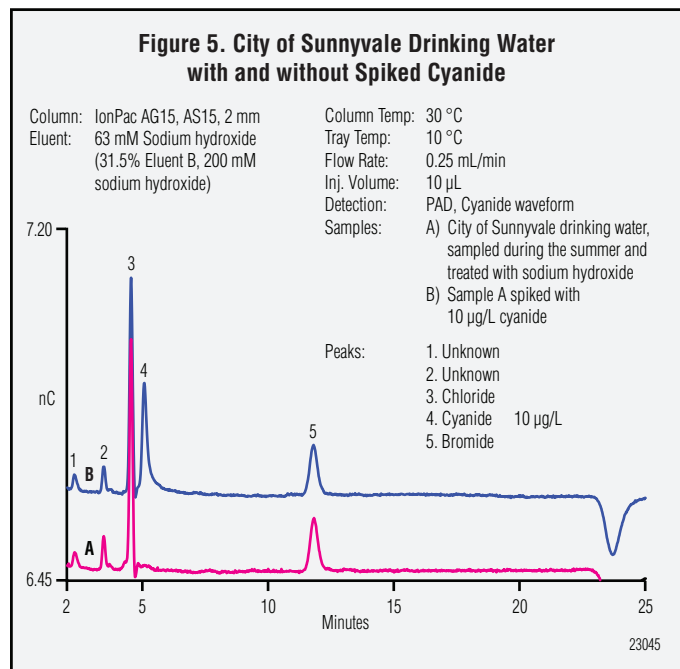
In Figure 4 we demonstrate the reproducibility and ruggedness of the cyanide method over 140 injections, ~ 62 h. During this study we measured cyanide in 10 µg/L cyanide standards and the same standards spiked in copper, iron, and nickel metal solutions pre-treated with OnGuard II H. The results showed that retention time and peak areas were stable over 62 h of the experiment. The retention time and peak area reproducibilities were  $5.78 \pm 0.027$  min and  $0.1232 \pm 0.0016$  nC-min, respectively.



In our studies, we evaluated the lifetime of five disposable silver working electrodes during the interference experiments, method qualification, and the testing of the municipal drinking water samples. Each electrode was installed, tested, and removed after two weeks of continuous use. The average peak area of 10 µg/L cyanide in 100 mM sodium hydroxide over the five electrodes was  $0.1206 \pm 0.0038$  nC-min, less than 1% variation. All five disposable silver working electrodes exceeded the guaranteed 14-day lifetime.

The characteristics of most drinking water change with the season. We determined free cyanide concentrations and spike recoveries of 5 and 10-µg/L cyanide in the City of Sunnyvale water throughout the course of our application experiments, and observed some changes.

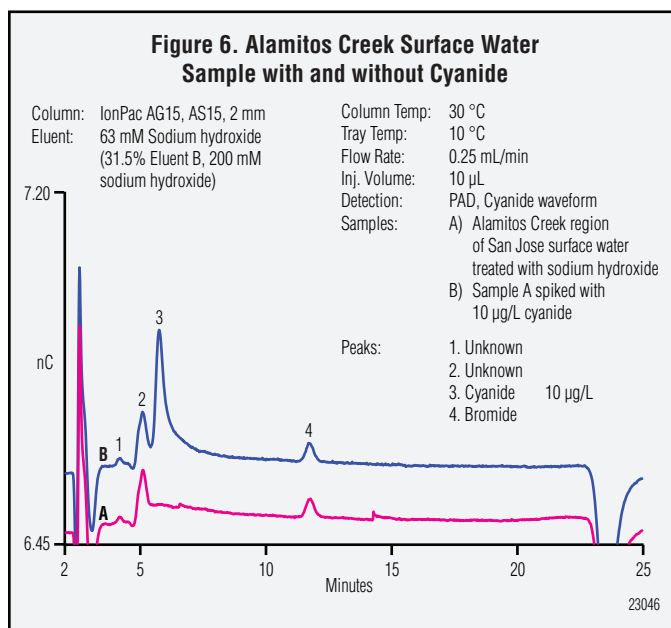
In Figure 5 we show good spike recovery of cyanide in the City of Sunnyvale water sampled during the summer,  $91.5 \pm 1.0\%$  ( $n=10$ ) and  $98.2 \pm 1.7\%$  ( $n=10$ ), for  $5 \mu\text{g/L}$  and  $10 \mu\text{g/L}$  of spiked cyanide, respectively. Cyanide also showed good recovery when  $10 \mu\text{g/L}$  of sulfide was added,  $91.9 \pm 1.7\%$ . Spiking cyanide into  $100 \text{ mM}$  sodium hydroxide yielded similar recoveries.



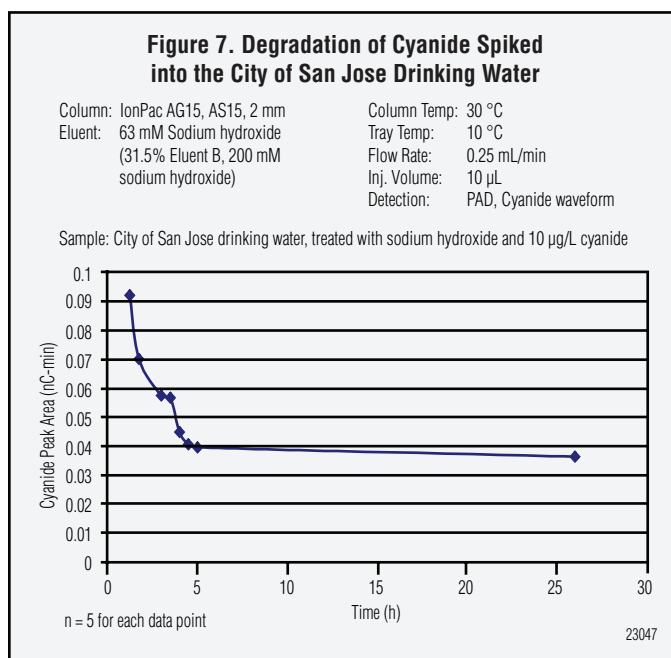
In Table 3, we show the free cyanide concentration and the recovery of cyanide from two drinking water samples including Sunnyvale water sampled in the fall and one surface-water sample (Alamitos Creek) from a mining region that was collected in the fall. Both city water samples had poor recovery. Only the Alamitos Creek surface water sample (Figure 6) exhibited acceptable recovery.

Table 3. Recovery of Cyanide from Untreated Drinking Water and Surface Water Samples <sup>a</sup>			
Concentration of Cyanide Spike (µg/L)	City of Sunnyvale Drinking Water <sup>a</sup>	City of San Jose Drinking Water	Alamitos Creek in Almaden
5	$9.6 \pm 3.0\%$	$74.3 \pm 11.8\%$	$102.0 \pm 1.3\%$
10	$55.5 \pm 2.8\%$	$99.6 \pm 0.5\%$	$97.3 \pm 2.4\%$

n = 5 for each sample  
<sup>a</sup>Sampled during the fall months



We speculated that City of Sunnyvale drinking water had changed since the initial sampling. The cyanide recovery from the City of San Jose drinking water over time showed a trend similar to those observed with metal interferences (Figure 7).



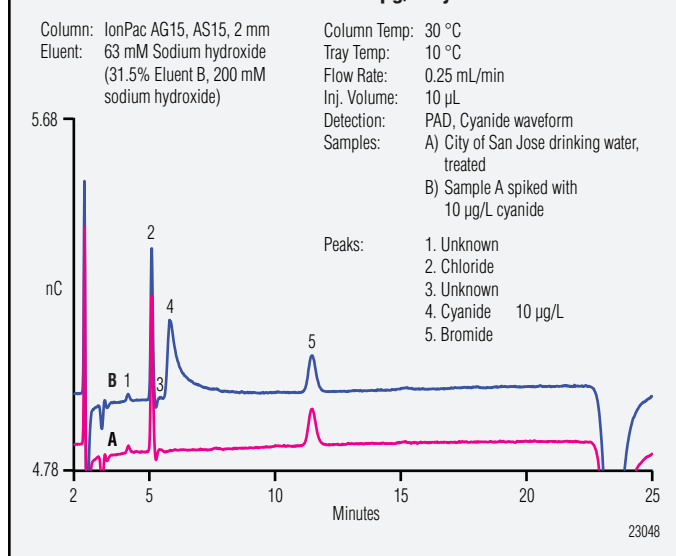
Therefore, we treated the samples with OnGuard II H cartridges and repeated the recovery experiments. We also analyzed drinking and surface water samples from Twain Harte Valley, an old gold mining region. The results (Table 4) show good recovery of 5 µg/L and 10 µg/L of cyanide in all samples, 80.6–95.9% and 93.1–99.5% (n=5), respectively. Cyanide in the treated samples was stable for 31 h, with >84% (n=5 for each sample) of the initial peak area response (Figures 8-9). No free cyanide was measured in any of the drinking or surface water samples

**Table 4. Recovery of Cyanide in Treated Water Samples<sup>a</sup> (OnGuard II H Cartridges)**

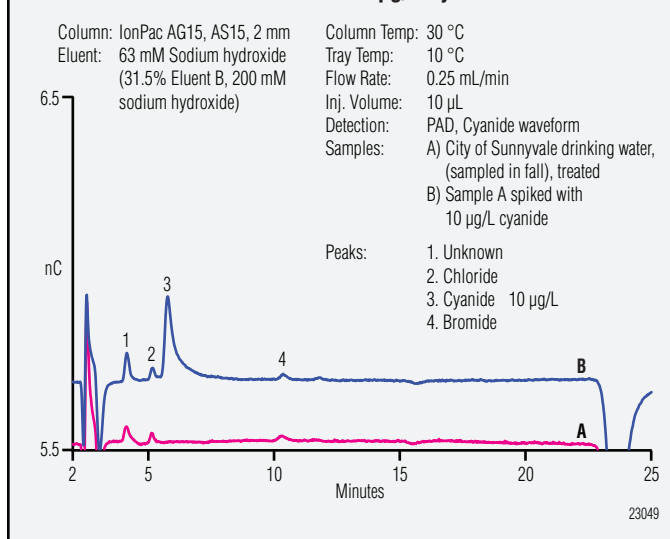
Concentration of Cyanide Spike (µg/L)	City of Sunnyvale Drinking Water	City of San Jose Drinking Water	Twain Harte Valley Drinking Water	Twain Harte Valley Flume
5	80.6 ± 5.5%	87.3 ± 6.4%	95.9 ± 2.5%	81.1 ± 3.2%
10	99.5 ± 2.8%	99.4 ± 2.5%	96.8 ± 3.1%	93.1 ± 1.5%

n = 5 for each sample  
<sup>a</sup>Sampled during the fall months

**Figure 8. Treated City of San Jose Drinking Water with and without 10 µg/L Cyanide**



**Figure 9. Treated City of Sunnyvale Drinking Water with and without 10 µg/L Cyanide**



## CONCLUSIONS

- Free cyanide can be determined in drinking water with IC-PAD.
- This method exhibits good sensitivity (MDL of 1 µg/L) and recovery and linearity from 2 to 100 µg/L.
- This method can tolerate basic-pH solutions; therefore we believe that this method can determine total cyanide without dilution or neutralization of pH 13 distillation samples.

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