

Determination of Total Cyanide in Wastewater and Drinking Water Samples by Ion-Exclusion Chromatography and Pulsed Amperometric Detection (ICE-PAD)

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INTRODUCTION

The U.S. EPA classifies cyanide as an inorganic contaminant for drinking water and surface water (U.S. National Primary Drinking Water Act), and wastewater (U.S. Clean Water Act). The EPA guidelines allow a maximum contamination level (MCL) of 200 µg/L of free cyanide in drinking water.¹

In wastewater, the EPA specifies cyanide discharge limits by industry and size of the facility (< 38,000 or > 38,000 liters per day). The typical sources of cyanide contamination are industrial waste from plating and mining industries, burning coal and plastics, and effluent from publicly owned treatment works (POTW).

The EPA specifies 5.2 µg/L total cyanide for POTW continuous discharges and 22 µg/L maximum discharges into fresh water. For discharges into salt water, the EPA specifies 1 µg/L total cyanide limits for both continuous and maximum discharges. The EPA defines these continuous (4 d) and maximum (1 h average) limits as exposure to aquatic life without deleterious effects.²

In POTWs, chlorination and chloramination processes used in waste treatment can generate cyanide in wastewater effluents.³ Nitrate formed from chlorination of ammonium creates unstable intermediates that degrade to cyanide during the harsh acid and temperature conditions typically used for acid-distillation in total cyanide determinations.³

Here, the authors describe an ion exclusion chromatography (ICE) method with pulsed amperometric detection (PAD) using a Pt disposable working electrode and an optimized waveform to determine total cyanide in drinking and wastewater samples.

The linearity, accuracy, precision, and robustness of this method are discussed here.

EXPERIMENTAL

Equipment

Dionex ICS-3000 chromatography system consisting of:

- SP Single Pump module, isocratic pump with degas option
- DC Detector/Chromatography module, single temperature zone
- ED Electrochemical Detector
- AS Autosampler with sample tray temperature controlling option
- Electrochemical cell
 - Combination pH/Ag/AgCl reference electrode
 - Disposable platinum (Pt) working electrode

Knitted reaction coil, 375 µL

Chromeleon® Chromatography Data System software

Sample Preparation

MICRO DIST® System for acid distillation of the samples

Samples

- Certified Wastewater Cyanide Standard, 40 µg/L total cyanide (High-Purity Standards) containing:
 - 20 µg/L Free cyanide from potassium cyanide and
 - 20 µg/L Complexed cyanide from potassium ferricyanide
 - 0.5% Potassium hydroxide diluent
- Municipal wastewater effluent without base and stabilized with base.
- Municipal drinking water stabilized with base.

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Conditions

Column:	IonPac® ICE-AG1 Guard, 4 × 50 mm IonPac ICE-AS1 Analytical, 4 × 250 mm
Flow Rate:	0.2 mL/min
Eluent:	50 mM Methanesulfonic acid
Column Temperature:	30 °C
Tray Temperature:	10 °C
Inj. Volume:	50 µL
Detection:	Pulsed Amperometric Detection (PAD)
Waveform:	See Table 1.
Reference Electrode:	pH-Ag/AgCl electrode in AgCl mode
Working Electrode:	Disposable Platinum
Typical Background:	70–120 nC
Noise:	20–30 pC
Run Time:	30 min

Table 1. Waveform Optimized for Acid Eluents⁴

Time (sec)	Potential vs Ag/AgCl (V)	Gain Region ^a	Integration	Ramp ^a
0.00	+ 0.30	Off	Off	Ramp
0.31	+ 0.30	On	Off	Ramp
0.32	+ 1.15	On	Off	Ramp
0.64	+ 1.15	On	On (Start)	Ramp
0.66	+ 1.15	On	Off (End)	Ramp
0.67	- 0.30	On	Off	Ramp
1.06	- 0.30	Off	Off	Ramp
1.07	+ 0.30	Off	Off	Ramp

Preparation of Samples

1. Sodium hydroxide (2 g of 50% sodium hydroxide solution per 1 L of sample) was added to the municipal drinking water sample.
2. The municipal wastewater effluent samples (untreated and treated with base) were filtered (0.2 µm, nylon) to remove bacteria and other particulates prior to acid digestion.
3. The certified wastewater sample was diluted 10-fold to the certified value of 4 µg/L of total cyanide prior to cyanide determinations.

Acid-Digestion Sample Preparation

1. The cyanide samples, 100 mM sodium hydroxide blanks, and cyanide control standards were digested according to EPA approved MICRO DIST Cyanide-1 Method, 10-204-00-1-X.⁵
2. The MICRO DIST user-filled collector tubes were rinsed with 1 mL each of acid and base solutions prior to use to minimize contamination.

RESULTS AND DISCUSSION

Separation

ICE is good for separating weakly disassociated acids, such as cyanide, from strongly dissociated acids (e.g., chloride).⁴

Figure 1 shows the chromatography of 5 µg/L cyanide in 100 mM sodium hydroxide and a blank (100 mM sodium hydroxide) prepared as described above.

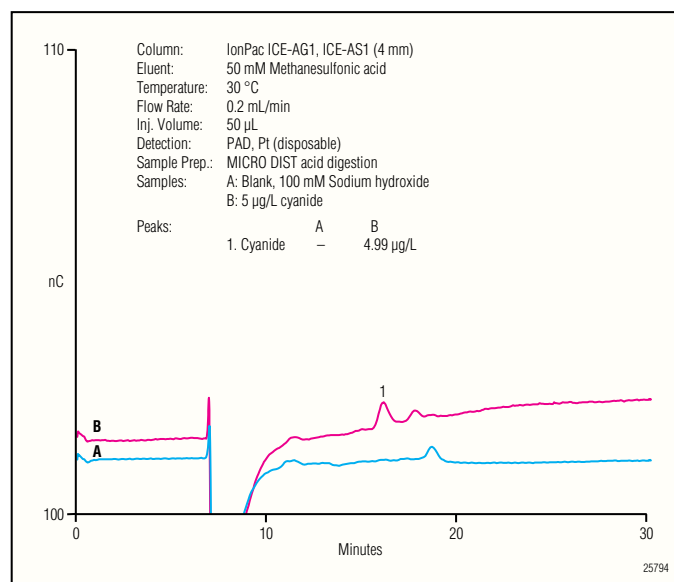


Figure 1. Comparison of A) blank and B) 5 µg/L cyanide standard.

Method Qualification

Table 2 shows the results of peak-to-peak noise, estimated limit of detection (LOD), linearity, and precision determinations.

Table 2. Method Qualification Parameters

Parameter	Results
Peak-to-Peak Noise ^a	19.8 pC
Estimated Limit of Detection (LOD) ^b	0.27 µg/L
Linearity ^c	1 - 25 µg/L, $r^2 = 0.9999$
Peak Area Precision ^d	0.98–2.94% RSD

^aPeak-to-peak noise was determined over three 60 min runs of deionized water injections.

^bLOD was based on the Student's *t*-test at 99% confidence limits ($n = 7$ of 0.50 µg/L cyanide standard).

^cLinearity was determined with triplicate injections of five standards.

^dPeak area precision was determined using six replicate injections each of 5 µg/L cyanide standard, 10-fold dilution of CWW sample with and without 5 µg/L added.

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Samples

We found 4.25 ± 0.07 $\mu\text{g/L}$ cyanide in a 10-fold dilution of the certified cyanide wastewater, 6.3% higher than the total cyanide certified value (Figure 2A).

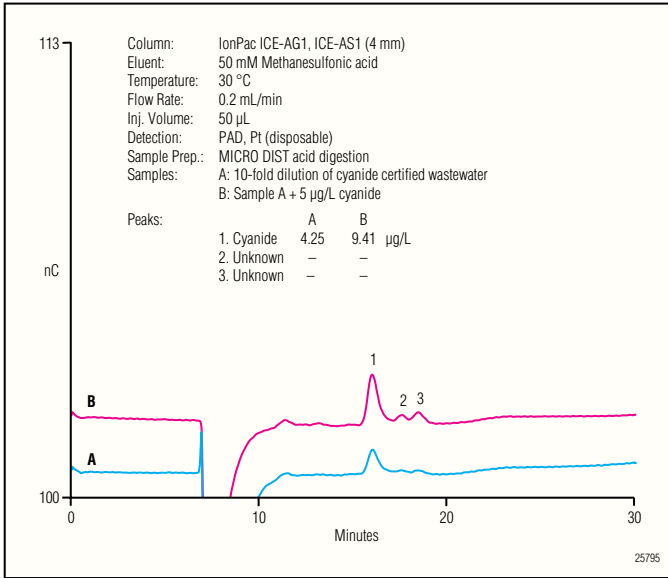


Figure 2. Comparison of A) 10-fold dilution of cyanide certified wastewater sample and B) sample A with 5 $\mu\text{g/L}$ cyanide added.

In the municipal drinking water sample, 0.67 ± 0.02 $\mu\text{g/L}$ ($n = 6$) total cyanide was detected (Figure 3A), well below the allowable limit.

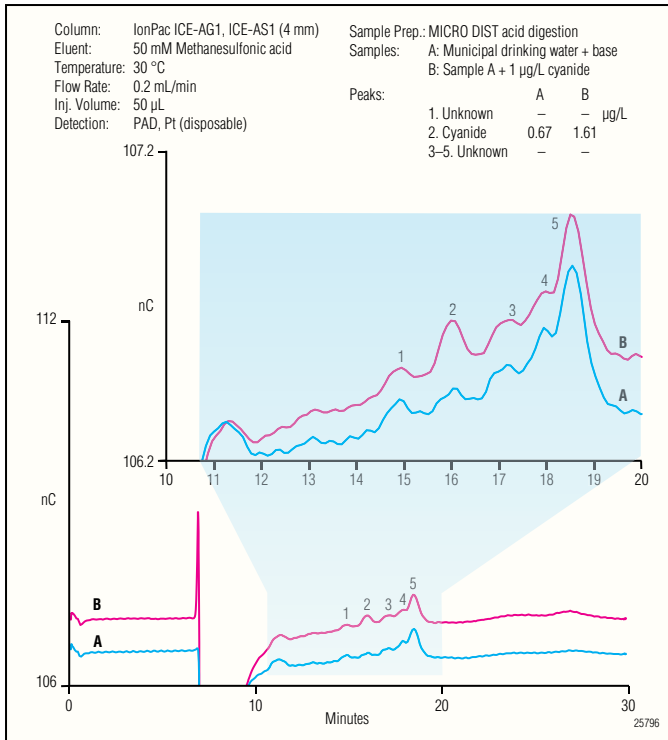


Figure 3. Comparison of A) Municipal drinking water and B) sample A with 1 $\mu\text{g/L}$ cyanide added.

The municipal wastewater effluent sample with and without base stabilization showed concentrations of 5.99 ± 0.09 $\mu\text{g/L}$ cyanide and $< \text{LOD}$, respectively (Figures 4B, 4A). These results agree with previous reports that chloramine and chlorine disinfectant treatments used in POTWs generate unstable cyanide intermediates, and that sodium hydroxide may stabilize these intermediates.^{3,7}

The average recoveries of cyanide over a three-day period were 97.4–101.8% ($n = 6$) (Figures 2B, 3B, 4C, Table 3).

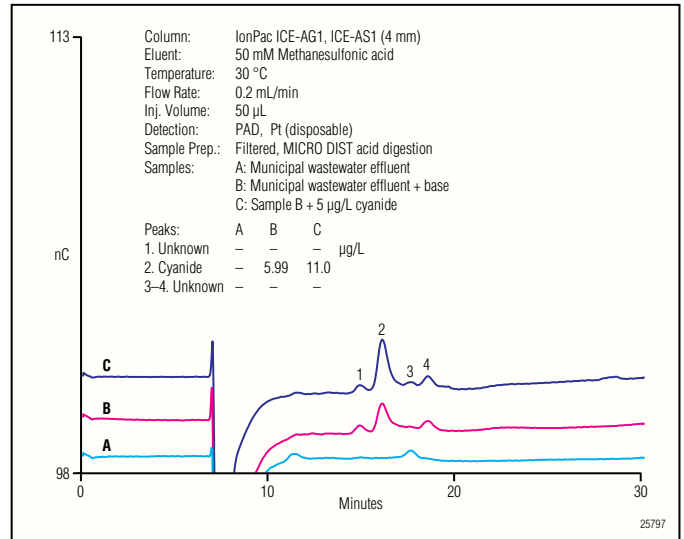


Figure 4. Comparison of A) Municipal wastewater effluent, B) second sample of municipal wastewater effluent with base added, and C) sample B with 5.0 $\mu\text{g/L}$ cyanide added.

Table 3. Average Cyanide Determinations in Samples Over Three Days

Sample	Amount Found ($\mu\text{g/L}$) ^a	Amount Added ($\mu\text{g/L}$)	Average Recoveries ^a (%)
100 mM Sodium hydroxide blank	$< \text{LOD}$	1.06	110.4 ± 6.4
Municipal drinking water	0.67 ± 0.02	0.99	97.4 ± 2.0
Filtered 100 mM sodium hydroxide	$< \text{LOD}$	5.02	102.3 ± 1.0
10-Fold dilution of certified cyanide wastewater sample (4.0 $\mu\text{g/L}$ total cyanide)	4.25 ± 0.07	4.99	101.8 ± 0.9
Filtered municipal wastewater effluent without base	$< \text{LOD}$	Not Tested	-
Filtered municipal wastewater effluent with base	5.99 ± 0.09	4.97	99.5 ± 1.0

^a $n = 6$

Interferences

- Table 4 shows the results of the interference experiments.
- Cyanate with or without thiocyanate or nitrate can generate cyanide during acid digestion.
- Individually, thiocyanate does not generate cyanide during acid digestion.

Robustness

- Table 5 shows the results of the robustness experiments. Increasing eluent concentration and changing columns had the most significant impact on the results.

CONCLUSION

- The method described here uses an ICE-PAD system method in conjunction with EPA approved Lachat MICRO DIST acid digestion system to accurately determine total cyanide in municipal water and wastewater effluent at µg/L concentrations.
- False positives for POTW chloraminated treated wastewater can occur (See Table 4) although these are independent of the chromatography method as they are also observed by other analysis methods.

REFERENCES

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2. Code of Federal Regulations, 40CFR413, 40CFR131, 40CFR132; Revised July 1, 2008, Fed Regist. **2008**; 214–215, 451–463, 493–494.
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6. Watershed Investigations, Laboratory Staff Watershed Protection Group Environmental Services Department City of San Jose. Cyanide Attenuation Study Report, 2004, 1–45.
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Table 4. Results of Testing Possible Interferences for Total Cyanide Determinations	
Sample	Average Cyanide Found (µg/L)
100 mM Sodium hydroxide blank	< LOD
5 µg/L Cyanide	5.03
ASTM challenge matrix ^a	32.32
Ammonium chloride, cyanate, and thiocyanate	21.29
Ammonium chloride, cyanate	26.31
Cyanate	16.21
Thiocyanate	< LOD

Table 5. Results of Robustness Experiments					
Parameter		Average Retention Time (min) ^a	Difference (%)	Peak Area (nC-min) ^a	Difference (%)
Eluent Concentration (mM MSA)	47.5	15.92	-0.3	0.377	-0.8
	50	15.96	–	0.380	–
	52.5	15.91	-0.3	0.344	-9.5
Column Temperature (°C)	28	16.01	+0.3	0.385	-1.3
	30	15.96	–	0.380	–
	32	15.89	-0.4	0.373	-1.8
Working Electrode	Conventional	15.96	0.0	0.382	+0.6
	Disposable, lot 080917	15.96	–	0.380	–
	Disposable, 2nd package, same lot	15.99	+0.2	0.376	-1.0
Column (Lot)	008-05-003	15.96	–	0.380	–
	008-05-092	16.68	+1.9	0.360	-5.2

^an = 6

Shaded areas = standard conditions

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