

# **Use of ASTM D 7284-08 “Standard Test Method for Total Cyanide in Water by Micro Distillation followed by Flow Injection Analysis with Gas Diffusion Separation and Amperometric Detection**

## **Introduction**

A new total cyanide method, ASTM D 7284-08, determines cyanide using traditional scaled down distillations and replaces pyridine barbituric acid colorimetry with gas-diffusion amperometry as the determinative step. The use of flow injection with gas diffusion and amperometric detection is also an optional determinative step utilized in ASTM D 2036-06 Test Method A. EPA already recognizes gas diffusion amperometry in two methods (OIA 1677 and ASTM D6888-04) for the analysis of available cyanide in CWA reporting and “free” cyanide under the SDWA. The method utilizes the same distillation currently performed in EPA 335.4 and/or LACHAT 10-204-00-1-X.

Approval of OIA 1677 for available cyanide demonstrated that gas-diffusion amperometry methods are capable of measuring certain cyanide species in wastewaters with complex matrices. The matrix of a total cyanide distillate, in the absence of certain interferences, is essentially a sodium hydroxide solution containing the cyanide ion, or “available” cyanide. Therefore, in the absence of interferences, pyridine barbituric acid colorimetry and gas-diffusion amperometry always obtain the same cyanide result. ASTM D 7284-08 was developed specifically for the analysis of samples that do contain interferences since these interferences bias the results from pyridine barbituric acid colorimetric methods. Specifically, ASTM D 7284-08 was developed to overcome low recoveries as a result of sulfide distilled into the absorber solutions, however, with further testing it was discovered that the method can overcome interferences from sulfite, thiosulfate, and thiocyanate as well.

## **Terminology**

**Total Cyanide** – Total cyanide is analytically defined and represents the sum of all inorganic chemical forms of cyanide that release free cyanide when refluxed under strong acid conditions. Total cyanide is

determined analytically by strong acid distillation or UV irradiation followed by determination of the free cyanide generated during the digestion. In water, total cyanide includes free cyanide, weak and dissociable metal – cyanide complexes, and strong metal cyanide complexes. Some of the strong metal complexes, such as those of gold, platinum, and cobalt, are not completely recovered.

**Distillation** – Samples are acidified with strong sulfuric acid in the presence of a magnesium chloride solution and boiled under reflux. Hydrogen Cyanide gas is generated and pulled/purged from the boiling acid solution through an absorber solution containing dilute sodium hydroxide.

**Pyridine – Barbituric Acid colorimetry** – The determinative step of “traditional” cyanide chemistry including EPA 335.4, Kelada 01, SM 4500, and LACHAT 10-204-00-1-X. The free cyanide ion in the absorber solution is converted to cyanogen chloride by reaction with chloramine T, which subsequently reacts with pyridine and barbituric acid to give a red-colored complex. Other compounds that co-distill with cyanide into the absorber solution, such as sulfide, sulfite, and volatile organics, also react with chloramine T resulting in positive or negative bias.

**Flow Injection Analysis (FIA) Gas Diffusion** – The small, uncharged HCN molecule passes through a micro porous hydrophobic membrane from the acidified sample solution into a continuous flowing stream of dilute sodium hydroxide solution. FIA gas diffusion methods are recognized by as approved techniques for matrix removal by EPA (OIA 1677 and ASTM D6888-04 for cyanide, and PAI – DK03 for TKN). Gas diffusion is also used in the LACHAT Micro Dist as a means to separate HCN from the steam distillate.

**Gas – Diffusion Amperometry** – The amperometric determination of CN cannot be separated from the gas diffusion step. The gas diffusion separates CN from ions, such as chloride, that would be measured by the cell. In the CN amperometric cell, the CN ion reacts with a silver electrode producing a signal that is proportional to cyanide concentration. The only known interference, sulfide, can be eliminated by use of complexing agents described in D 7284-08 and D 6888-04 prior to the gas diffusion process that prevent hydrogen

sulfide from diffusing. The only reagent required for the gas diffusion amperometric detection of CN is dilute sodium hydroxide.

### Species Dependent Recoveries

Total distillations of 15 cyanide species (midi distillation according to EPA 335.4) at 200 ppb CN were carried out in triplicate. The concentration of cyanide in the absorber solution was determined simultaneously by pyridine barbituric acid colorimetry (EPA 335.4) and gas-diffusion amperometry (ASTM D 7284-08). Table I summarizes the species dependent cyanide recoveries obtained.

**Table I** Species Dependent Cyanide % Recoveries <sup>a, b</sup>

Species	ASTM D 7284-08	EPA 335.4
$[\text{Zn}(\text{CN})_4]^{-2}$	101 (1.0)	101 (1.1)
$[\text{Cd}(\text{CN})_4]^{-2}$	101 (1.8)	99.0 (1.3)
$[\text{Cu}(\text{CN})_4]^{-2}$	102 (1.5)	100 (1.0)
$[\text{Ag}(\text{CN})_2]^{-1}$	99.0 (2.5)	100 (0.9)
$[\text{Ni}(\text{CN})_4]^{-2}$	102 (1.7)	103 (0.3)
$[\text{Hg}(\text{CN})_4]^{-2}$	104 (1.0)	100 (0.3)
$\text{Hg}(\text{CN})_2$	99.5 (0.3)	98.5 (0.6)
$[\text{Fe}(\text{CN})_6]^{-4}$	99.5 (0.5)	99.6 (0.8)
$[\text{Fe}(\text{CN})_6]^{-3}$	100 (0.8)	100 (0.3)
$[\text{Pd}(\text{CN})_4]^{-2}$	70.0 (3.0)	71.0 (3.2)
$[\text{Au}(\text{CN})_2]^{-1}$	55.0 (0.9)	56.0 (1.0)
$[\text{Ru}(\text{CN})_6]^{-2}$	45.0 (0.6)	47.0 (0.6)
$[\text{Pt}(\text{CN})_4]^{-2}$	0.0	0.0
$[\text{Pt}(\text{CN})_6]^{-2}$	0.0	0.0
$[\text{Co}(\text{CN})_6]^{-3}$	0.0	0.0

<sup>a</sup> % Relative Standard Deviation (n=3) in parenthesis

<sup>b</sup> Solujic Ljiljana, *Research Report prepared for OI Analytical*, University of Nebraska

Table I demonstrates that in the absence of interferences EPA 335.4 and ASTM D 7284-08 obtain exactly (within experimental error) the same result. This is because the sample pre-treatment (distillation) is the same for both methods, and the measurement steps (colorimetry and FIA gas diffusion – amperometry) are measuring the free sodium cyanide that was trapped in the absorber solution.

## Interferences

A series of 18 potential interferences (at 200 mg/L) were subjected to the “total cyanide distillation” as described in EPA 335.4, and then simultaneously analyzed by pyridine barbituric acid colorimetry (EPA 335.4) and FIA gas diffusion amperometry (ASTM D 7284-08). When the method pretreatments described in EPA 335.4 are performed, no interferences are detected when cyanide is not present (see Table II). When these potential interferents (at 200 mg/L) are distilled together with cyanide (at 0.2 mg/L) incomplete recoveries are obtained with both measurements. These low recoveries are due to interferences caused by the distillation process (see Table III).

**Table II** Response of Potential Interferents to EPA 335.4 and ASTM D 7284-08 <sup>a</sup>

Interfering Species	ASTM D7284-08 (µg CN <sup>-</sup> /L)	EPA 335.4 (µg CN <sup>-</sup> /L)
Chloride (Cl <sup>-</sup> )	0.0	0.0
Bromide (Br <sup>-</sup> )	0.0	1.4
Iodide (I <sup>-</sup> )	0.0	2.2
Sulfate (SO <sub>4</sub> <sup>-2</sup> )	0.0	1.4
Sulfite (SO <sub>3</sub> <sup>-2</sup> )	0.0	0.0
Carbonate (CO <sub>3</sub> <sup>-2</sup> )	0.0	0.0
Hypochlorite (OCl <sup>-</sup> )	0.0	0.0
Cyanate (OCN <sup>-</sup> )	0.0	0.0
Nitrate (NO <sub>3</sub> <sup>-</sup> )	0.0	0.0
Nitrite (NO <sub>2</sub> <sup>-</sup> )	0.0	0.0
Ammonium (NH <sub>4</sub> <sup>+</sup> )	0.0	0.0
Acetaldehyde (CH <sub>3</sub> CHO)	0.0	0.0
Glucose (C <sub>3</sub> H <sub>8</sub> O <sub>3</sub> )	0.0	0.0
Glycerol (C <sub>6</sub> H <sub>12</sub> O <sub>6</sub> )	0.0	0.0
Ascorbic Acid (C <sub>6</sub> H <sub>8</sub> O <sub>6</sub> )	0.0	0.0
Thiocyanate (SCN <sup>-</sup> )	0.0	0.0
Thiosulfate (S <sub>2</sub> O <sub>3</sub> <sup>-2</sup> )	0.0	0.0
Sulfide (S <sup>-2</sup> )	0.0	0.0

<sup>a</sup> Solujic Ljiljana, *Research Report prepared for OI Analytical*, University of Nebraska, 1997

The same 18 potential interferents (at 200 mg/L) were distilled according to the distillation procedure described in EPA 335.4 in the presence of cyanide (at 0.2 mg/L). Method pretreatments were performed exactly as described in the EPA procedure and then cyanide concentrations in the distillate were determined simultaneously by pyridine barbituric acid colorimetry (EPA 335.4) and FIA gas diffusion amperometry (ASTM D7284-08). Data is presented in Table III. Low recoveries for distillations containing sulfide, sulfite, thiocyanate, and thiosulfate can be attributed, in part, to interferences that occur either in sample preservation or in the distillation step itself (see ASTM D 7365 “Standard Practice for Sampling, Preservation, and Mitigating Interferences in Water Samples for Analysis of Cyanide”). However, it must be noted that significant negative bias also results in the pyridine barbituric acid measurement of cyanide in samples that contain sulfide, sulfite, thiosulfate, and/or thiocyanate. This interference is a result of either evolution of  $\text{H}_2\text{S}$  and entrapment in the absorber solution, or  $\text{SO}_2$  generation during distillation and subsequent absorption as  $\text{SO}_3^{2-}$  (sulfite) in the absorber solution. Sulfite is listed as an interferent in most colorimetric cyanide methods including SM 4500, ASTM D2036, and Kelada 01. Since sulfite interferes by increasing the chloramine T demand, negative bias due to its presence will likely go undetected by automated colorimetric methods such as EPA 335.4 or Kelada 01.

**Table III** Concentration of  $\text{CN}^-$  in absorber solutions after EPA 335.4 “total cyanide distillations” containing 200-mg/L possible interferent and 200  $\mu\text{g/L}$   $\text{CN}^-$  obtained with pyridine barbituric acid colorimetry (EPA 335.4) and FIA gas diffusion amperometry (ASTM D 7284-08). Sample pretreatment is done exactly according to EPA 335.4.<sup>c</sup>

Interfering Species	ASTM D7284-08* ( $\mu\text{g CN}^-/\text{L}$ )	EPA 335.4 ( $\mu\text{g CN}^-/\text{L}$ )
Chloride ( $\text{Cl}^-$ )	201	199
Bromide ( $\text{Br}^-$ )	202	200
Iodide ( $\text{I}^-$ )	199	196
Sulfate ( $\text{SO}_4^{-2}$ )	205	202
Sulfite ( $\text{SO}_3^{-2}$ ) <sup>a</sup>	0.0	0.0
Carbonate ( $\text{CO}_3^{-2}$ )	206	207
Hypochlorite ( $\text{OCl}^-$ ) <sup>a</sup>	129	139
Cyanate ( $\text{OCN}^-$ )	202	205
Nitrate ( $\text{NO}_3^-$ )	204	205
Nitrite ( $\text{NO}_2^-$ )	226	203
Ammonium ( $\text{NH}_4^+$ )	203	206
Acetaldehyde ( $\text{CH}_3\text{CHO}$ )	194	184
Glucose ( $\text{C}_3\text{H}_8\text{O}_3$ )	198	198
Glycerol ( $\text{C}_6\text{H}_{12}\text{O}_6$ )	196	205
Ascorbic Acid ( $\text{C}_6\text{H}_8\text{O}_6$ )	192	186
Thiocyanate ( $\text{SCN}^-$ ) <sup>b</sup>	160	151
Thiosulfate ( $\text{S}_2\text{O}_3^{-2}$ ) <sup>a</sup>	0.0	0.0
Sulfide ( $\text{S}^{-2}$ ) <sup>a</sup>	0.0	0.0

\* Sample pretreatment according to EPA 335.4 for comparison of FIA gas diffusion amperometry. ASTM D7284-08 includes enhanced interferent treatment that minimizes interferences. These enhancements increase cyanide recoveries in the presence of sulfide, sulfite, and thiosulfate.

<sup>a</sup> Cyanide ion is rapidly lost during sample preservation, or during the distillation process. Methods cannot correct for cyanide lost during sampling. ASTM D7284-08 includes pretreatments to maximize cyanide recovery. For comparison, these pretreatments were not included as part of this table. See Tables in later sections of this report.

<sup>b</sup> Thiocyanate alone results in a negative bias. Thiocyanate distilled with nitrate can result in significant positive bias with both methods; however, this interference can be minimized with D 7284-08 with sample pretreatment.

<sup>c</sup> Solujic Ljiljana, *Research Report prepared for OI Analytical*, University of Nebraska, 1997

## Individual Interferences

### Sulfide

Sulfide is listed as an interference in all cyanide analysis methods. Sulfide removal methods based on precipitation as sulfide salts are generally ineffective. Cadmium salts (EPA 335.4) combine with soluble iron cyanide complexes forming a very stable cadmium iron cyanide species resulting in low recoveries. Lead Carbonate (Standard Methods 4500 and ASTM D2036) reacts with sulfide to form lead sulfide. The lead sulfide reacts rapidly converting cyanide to thiocyanate within minutes<sup>1</sup>. Other precipitation methods such as use of bismuth (SW 846 9010C), and sulfide removal based on selective volatilization of H<sub>2</sub>S (40CFR Part 136 Table II footnotes) are also ineffective. Table IV lists some sulfide removal (200 mg/L S<sup>-2</sup>) procedures and typical recoveries for total cyanide.

**Table IV** Total Cyanide Recovery after removal of 200 mg/L S<sup>-2</sup> by various procedures<sup>a</sup>. Analysis by ASTM D 7284-08 / D 6888-04

<b>Sulfide Removal Method</b>	<b>Recovery</b>
Control (no dilution) with 4X strength sulfide abatement reagent as specified in D 7284-08	99.5 %
Control (10 X dilution) regular strength sulfide abatement reagent as specified in D 7284-08	100 %
Cadmium Salt precipitation	69 %
Zinc Salt precipitation	28 %
Bismuth Salt precipitation	57 %
Dynamic Stripping <sup>b</sup>	74 %
Headspace Expelling <sup>b</sup>	69 %
Lead Carbonate precipitation	76.5 %
Lead Acetate addition	74.5

<sup>a</sup> Source – ASTM D19.06 Research Report presented at ASTM/EPA Cyanide Workshop in June 2008

<sup>b</sup> Sulfide still detectable above 50 ppm.

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<sup>1</sup> Wilmot and others, *Formation of Thiocyanate During Removal of Sulfide as Lead Sulfide Prior to Cyanide Determination*, Analyst, June 1996, Vol 121 (799 – 801)

The data in Table IV demonstrates that the only effective sulfide removal methods are the on-line sulfide abatement reagents that are an integral part of ASTM D6888-04, a modified OIA 1677, and ASTM D 7284-08. This reagent removes sulfide prior to the gas diffusion preventing it from interfering with cyanide detection. Though the method reagents can be modified to compensate for sulfide at up to 200 mg/L, data collected by ASTM D19.06 and others demonstrates cyanide is not stable in the presence of sulfide at concentrations greater than about 50 mg/L.

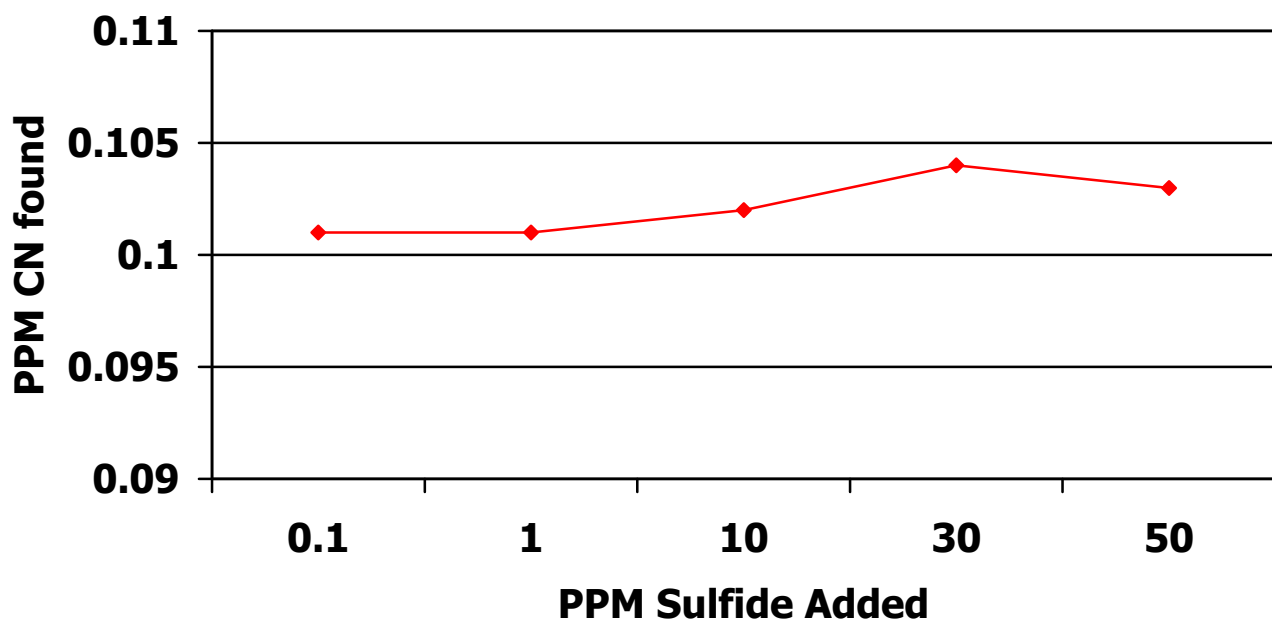
Sulfide interferes with Ion Selective Electrode (ISE), titrimetric, and colorimetric methods at concentrations below 50 mg/L. The Kelada 01 method suggests diluting samples if sulfide exceeds 10 mg/L. Standard Methods 4500 and EPA 335.4 only mention removal of sulfide below detectable by lead acetate test strips ( $\sim 50 \text{ mg/L S}^{-2}$ ), however, Sebroski and Bogren<sup>2</sup> reported that significant problems with colorimetric measurement of cyanide in sulfide containing wastewater samples were successfully overcome using the on-line sulfide abatement reagents utilized in the FIA gas diffusion amperometric methods (see Figure 1).

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<sup>2</sup> Sebroski, John R., and Bogren, Karen L., *An NPDES Distillation Method for Measuring Total Cyanide in Water*, American Laboratory, October 2005,



**Figure 1** Plot of Cyanide recoveries in the presence of Sulfide by FIA gas diffusion amperometry and sulfide abatement reagents



### Sulfite

Sulfite is listed as an interference with colorimetric determination of cyanide in Standard Methods for the Examination of Water and Wastewater, and ASTM D2036. Sulfite in total cyanide absorber solutions reacts with chloramine T increasing its demand. Standard Methods and ASTM D2036 suggest checking sample solutions after chloramine T addition to verify the presence of excess chlorine. While possible with manual colorimetric methods, checking residual chlorine levels on each sample is not possible with automated methods such as EPA 335.4 or Kelada 01. The Kelada 01 method does not specifically mention sulfite as an interferent, however, the Kelada 01 method does mention that sulfite was evaluated as a treatment for oxidizers and in the process found to interfere with the method.

According to Standard Methods 4500 – CN B some wastewaters, such as those from coal gasification or chemical extraction mining, contain high

levels of sulfite<sup>3</sup>. Sulfite is also used extensively as a dechlorination agent for treating wastewater disinfected by chlorination<sup>4</sup>. In other words, sulfite is a likely constituent of water samples slated for cyanide analysis. Table V compares results of “total cyanide” determined according to the listed methods. Since there is a lack of laboratories performing the Kelada 01 method, a laboratory analyzing cyanide by EPA method 335.3 was used. EPA 335.3 is similar to the Kelada 01 method utilizing UV irradiation, followed by distillation and pyridine barbituric acid colorimetry.

**Table V** Comparison of Total Cyanide Recovery by Various Distillation Methods in the Presence of 200mg/L Sulfite <sup>a</sup>

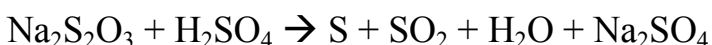
<b>ASTM D2036 / SM 4500-CN C</b>	<b>EPA 335.3 (automated)</b>	<b>ASTM D 7284-08</b>
98 %*	0.0 %	94 %

\* Sample solutions containing sulfite must not be preserved with NaOH or low recoveries will result.

<sup>a</sup> Source – ASTM D19.06 Research Report presented at ASTM/EPA Cyanide Workshop in June 2008

### Thiosulfate

Thiosulfate reacts with acid solution according to the following reaction:



The products for the reaction between thiosulfate and acid solution include native sulfur and sulfur dioxide. Native sulfur is a listed interference (40 CFR Part 136 Table II footnotes) for cyanide analysis reacting quickly with cyanide to form thiocyanate and lowering recoveries. Sulfur dioxide is volatile, distills into absorber solutions and becomes sodium sulfite. We have listed interferences associated with sulfite above. Therefore, thiosulfate interferes with colorimetric cyanide determinations in a similar manner as sulfite. ASTM D2036 mentions sulfur oxides as a potential interference without specifically naming thiosulfate, and Standard Methods 4500

<sup>3</sup> Standard Methods for the Examination of Water and Wastewater, *Method 4500-CN B Preliminary Treatment of Samples*, Standard Methods On-line, accessed September 2008.

<sup>4</sup> MacCrehan, Jensen, and Helz, *Detection of Sewage Organic Chlorination Products That are Resistant to Dechlorination with Sulfite*, Environ. Sci. and Technology, 32(22), 3640 – 3645, 1998

specifies using thiosulfate for removal of oxidizers. Kelada 01 does not mention thiosulfate as an interferent, however, in the section on treatment of oxidizers the Kelada method mentions that thiosulfate was evaluated and found to interfere with the method. Table VI compares “total cyanide” determined by the listed methods. Since there is a lack of laboratories performing the Kelada 01 method, a laboratory analyzing cyanide by EPA method 335.3 was used. EPA 335.3 is similar to the Kelada 01 method utilizing UV irradiation, followed by distillation and pyridine barbituric acid colorimetry.

**Table VI** Comparison of Total Cyanide % Recovery by Various Distillation Methods in the Presence of 200mg/L Thiosulfate <sup>a</sup>

<b>ASTM D2036 / SM 4500-CN C</b>	<b>EPA 335.3 (automated)</b>	<b>ASTM D 7284-08</b>
84.5 %*	83.5 %	94 %

\* 84.5% recovery obtained after addition of extra chloramine T during color development. If extra chloramine T were not added, recovery would have been lower.

<sup>a</sup> Source – ASTM D19.06 Research Report presented at ASTM/EPA Cyanide Workshop in June 2008

### Thiocyanate

As seen in Table III, thiocyanate can react under the acid conditions of total cyanide distillations and decrease cyanide recoveries. Thiocyanate can also, however, react with oxidizers such as nitrate producing significant false positives during cyanide distillations. Sulfamic acid, often added to decrease interferences from nitrate and nitrite, reduces but does not eliminate the false positive results generated by the distillation of thiocyanate in the presence of nitrate (Table VII). Thiocyanate and nitrate are both common contaminants in wastewater samples requiring cyanide analysis (see Table VIII). The nitrate concentration in wastewater effluents is typically 15 – 20 mg/L as NO<sub>3</sub> – N<sup>5</sup> also, since the “false” recoveries of cyanide from thiocyanate and nitrate are reproducible spike recoveries cannot be used as an indicator for demonstrating the accuracy of a cyanide distillation (Table IX).

<sup>5</sup> Metcalf and Eddy, Inc. 1991 *Wastewater Engineering: Treatment, Disposal, and Reuse*, 3<sup>rd</sup> Edition. McGraw-Hill, Inc., New York

**Table VII** Thiocyanate Interference in Cyanide Analysis When Nitrate is Present in a Reagent Water Matrix<sup>6</sup>

Experiment #	SCN- (mg/L)	NO3- (mg/L)	Total CN by SM 4500 (mg/L)
1	0.1	1.0	<0.002
2	0.1	10.0	0.010
3	0.1	25.0	0.017
4	0.1	50.0	0.060
5	0.1	100	0.086
6	1.0	10.0	0.009
7	1.0	50.0	0.038

**Table VIII** Industrial Sources of Water and Thiocyanate Concentration <sup>a</sup>

Industrial Source	mg SCN <sup>-</sup> / L
Coke plant ammonia still effluent	554
Coke plant ammonia still effluent after biological treatment	36
Coke plant ammonia still effluent	200
Coke plant ammonia still effluent after biological treatment	< 1
Blast furnace	1.3
Chemical plant wastewater	50.5
Chemical plant wastewater	10.4
Coke plant wastewater	23.6
Oil refinery wastewater	2.24
Oil refinery sour water stripper effluent	16
Metal plating wastewater effluent	0.02

<sup>a</sup> Dzombak, Ghosh, and Wong-Chong, Cyanide in Water and Soil Chemistry Risk and management, CRC Press, 2006

<sup>6</sup> Kavanaugh, Dzombak, Theis, Young, and Luthy, *Cyanide Formation and Fate in Complex Effluents and its relation to water Quality Criteria*, Water Environment Research Foundation, 2003

**Table IX** Comparison of Total Cyanide Results and Spike Recovery in a Synthetic Sample that does not contain cyanide <sup>a</sup>.

	<b>SM 4500-CN C</b>	<b>EPA 335.3</b>	<b>ASTM D7284 - 08</b>
Sample Result (µg/L CN)	32	16	ND <sup>b</sup>
200 µg/L CN Spike Result	228	211	206
Recovery	98 %	98 %	103 %

<sup>a</sup> Source – ASTM D19.06 Research Report presented at ASTM/EPA Cyanide Workshop in June 2008

<sup>b</sup> ND = Not Detected above 10 µg/L CN<sup>-</sup>.

ASTM Method D7284-08 overcomes false positives due to interferences from thiocyanate including thiocyanate in the presence of nitrate. In a single laboratory study (reported at the ASTM/EPA Cyanide Workshop June 2008) less than 0.002 mg /l CN and a 91 % Spike Recovery was obtained in a “challenge” matrix containing 25 mg/L NO<sub>3</sub> – N and 15 mg/L SCN<sup>-</sup>. This “challenge matrix” is especially problematic resulting in false positive cyanide results by “total cyanide” distillation methods.

## Analysis of “Real World” Samples

Triplicate “total cyanide” distillations of 9 real world samples and analysis of the absorber solutions by pyridine barbituric acid colorimetry (EPA 335.4) and FIA gas diffusion amperometry (ASTM D7284-08) were performed to demonstrate equivalency of the two methods. The results obtained are given in Table X.

Table X “Total Cyanide” results for “real world” samples obtained by colorimetric (EPA 335.4) and FIA gas diffusion amperometry (ASTM D7284-08) methods <sup>a</sup>.

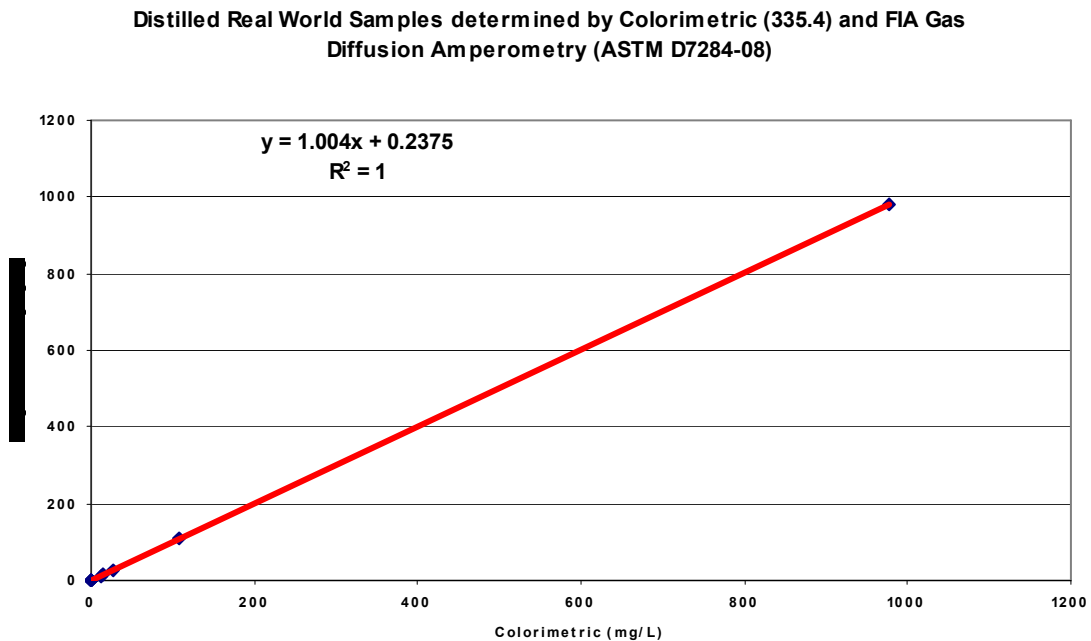
Sample	EPA 335.4 (mg CN/L)	ASTM D7284-08 (mg CN/L)
1	0.045 (13) <sup>b</sup>	0.044 (12)
2	108 (1.1)	110 (0.9)
3	12.5 (0.9)	12.2 (0.9)
4	0.026 (5.1)	0.025 (5.5)
5	0.005 (3.5)	0.005 (2.0)
6	14.5 (1.0)	14.4 (1.4)
7	978 (1.6)	982 (1.1)
8	26.0 (1.6)	27.1 (2.2)
9	0.269 (2.6)	0.271 (2.4)

<sup>a</sup> Solujic Ljiljana, *Research Report prepared for OI Analytical*, University of Nebraska, 1997

<sup>b</sup> % Relative Standard Deviation (n=3) in parenthesis

The same data presented in Table X is plotted graphically in Figure 2. The slope of 1.004 verifies that the data is essentially identical.

**Figure 2** Scatter Plot demonstrating correlation of “total cyanide” data collected by colorimetry (EPA 335.4) and FIA gas diffusion amperometry (ASTM D7284-08)



### **D7284-08 Precision and Bias Study**

The instrumental portion of ASTM D 7284-08 is based on test method D 6888-04 and is expected to have similar performance. D 7284-08 was evaluated and validated in a single laboratory to meet the requirements of ASTM D 2777-06. The precision and bias data are shown in tables XI and XII.

**Table XI** Precision and Bias in Laboratory Water and Synthetic Wastewater, SM-990-011. Samples fortified with  $\text{K}_3\text{Fe}(\text{CN})_6$  as  $\text{CN}^-$ , and results are reported as  $\mu\text{g/L}$  (ppb).

Replicate	Water			SM-990-011*		
	20 ppb	100 ppb	300 ppb	20 ppb	100 ppb	300 ppb
1	21.5	105	301	23.2	107	284
2	22.0	108	298	22.5	105	300
3	21.7	107	305	23.0	106	306
4	21.7	104	311	22.6	108	305
5	22.1	106	305	22.7	109	306
6	19.4	106	304	22.2	106	320
7	21.8	105	299	22.3	109	305
Std Deviation	0.929	1.35	4.42	0.360	1.57	10.7
Mean	21.5	106	303	22.6	107	304
RSD %	4.33	1.27	1.46	1.59	1.47	3.51
Recovery %	107	106	101	113	107	101

\*2% (volume/volume) synthetic precious metals mining wastewater prepared from SM-990-011, High Purity Standards, Charleston, SC. Prepared sample contains 0.3 mg/L  $\text{SCN}^-$ , 0.5 mg/L  $\text{OCN}^-$ , 0.5 mg/L  $\text{NH}_3$  as N, and 0.5 ppm  $\text{NO}_3$  as N.



**Table XII** Precision and Bias in Selected Matrices

Samples fortified with 100 µg/L K<sub>3</sub>Fe(CN)<sub>6</sub> as CN<sup>-</sup>. Results reported in µg/L (ppb).

<b>Sample / Replicate</b>	<b>POTW Effluent*</b>	<b>Creek Water</b>	<b>Metals Finishing Wastewater</b>
Background	ND	9.65	8.89
Background	ND	9.79	9.11
Mean Background	0	9.72	9.00
Spike 1	81.2	105	102
Spike 2	89.1	108	103
Spike 3	85.0	108	103
Spike 4	88.6	111	105
Spike 5	87.6	110	106
Spike 6	89.6	108	102
Spike 7	88.6	107	106
Std Deviation	3.01	1.95	1.77
Mean	87.1	108	104
RSD %	3.45	1.80	1.71
Recovery %	87.1	97.3	94.9
*POTW = Publicly owned treatment works. Ascorbic acid added to POTW effluent during sample collection			

### Two Column Comparisons for ASTM D7284-08 and EPA 335.4

TOPIC	EPA 335.4	ASTM D7284-08
Scope and Application	This method covers the determination of cyanide in drinking, ground, surface, and saline waters, domestic and industrial wastes. The applicable range is 5 to 500 µg/L.	This test method is used to determine the concentration of total cyanide in an aqueous wastewater or effluent. The applicable range is 2 to 400 µg/L. Higher concentrations may be analyzed by sample dilution or a lower injection volume.
Summary of Method	<p>The cyanide as HCN is released from cyanide complexes by means of a manual reflux – distillation operation and absorbed in a scrubber containing sodium hydroxide solution.</p> <p>The cyanide ion in the absorber solution is converted to cyanogen chloride by reaction with chloramine T, which subsequently reacts with pyridine barbituric acid to give a red-colored complex.</p>	<p>The samples are distilled with strong acid in the presence of magnesium chloride catalyst and captured in a sodium hydroxide absorber solution.</p> <p>The cyanide ion in the absorber solution is introduced into a flow injection analysis system where the cyanide ion is acidified to form HCN. The HCN diffuses through a micro porous hydrophobic membrane into an alkaline acceptor stream. An amperometric flow cell detector measures the cyanide in the acceptor stream. The measurement technique used to measure the free cyanide ion in the “total” cyanide</p>

		distillation absorber solutions is based on EPA approved “free” or available cyanide methods OIA 1677 and ASTM D6888
Interferences	<p>Aldehydes, nitrate + nitrite, oxidizers, thiocyanate, thiosulfate, sulfite, and sulfide can cause positive or negative interference.</p> <p>Sulfide adversely affects the procedure by producing hydrogen sulfide during distillation. Sulfide is precipitated using cadmium and the precipitation is repeated till sulfide is no longer detected by lead acetate strips (~50 ppm S).</p> <p>Nitrate + Nitrite interferences are minimized by addition of sulfamic acid.</p> <p>Oxidizing agents are removed by ascorbic acid or sodium arsenite.</p>	<p>Refer to ASTM D 7365 for proper sampling and preservation of cyanide.</p> <p>Aldehydes and oxidizers must be treated at sample collection.</p> <p>Sulfide at concentrations below 50 ppm does not interfere. Dilute sample with sulfide above 50 ppm.</p> <p>Sulfite, Thiosulfate, and Thiocyanate can potentially interfere causing negative bias as a result of the distillation process; these interferences are minimized with the detection used in D 7284-08. The Sulfite ion does not interfere with cyanide detection.</p> <p>False positives as a results of thiocyanate and nitrate are minimized with this method.</p>

Equipment and Supplies	<p>Glass Midi distillation apparatus for cyanide</p> <p>Continuous Flow Analyzer equipped for mixing color reagents and measurement with a photometric detector</p>	<p>Glass Midi Distillation apparatus, or LACHAT MicroDist apparatus and sample tubes for Cyanide</p> <p>Continuous Flow Analyzer equipped for Gas diffusion and an amperometric detector</p>
Calibration and Standardization	Calibrated Range is 5 – 500 µg/L CN	Calibrated Range is 2 – 400 µg/L CN
Procedure	<p>Treat samples for interferences and distill 50 ml in sulfuric acid – magnesium chloride solution. Purge through an absorber solution containing 0.25 N Sodium Hydroxide.</p> <p>Boil for 1.5 hours, turn off heat, and then continue for 15 minutes.</p> <p>Analyze “free” cyanide ion in the absorber using automated pyridine barbituric acid colorimetry</p>	<p>Treat samples for interferences and distill 50 ml (midi distillation) or 6 ml (Microdist) in sulfuric acid – magnesium chloride solution. Midi distillations are purged through an absorber containing 0.25 N Sodium Hydroxide. Microdist diffuses HCN generated through a hydrophobic membrane where CN is absorbed into 0.25 N Sodium Hydroxide.</p> <p>Analyze “free” cyanide ion in the absorber solution using Flow Injection Gas Diffusion Amperometry. The determination step is similar to ASTM D6888-04 or OIA 1677 “free” and available cyanide methods.</p>

Safety	<p>Pyridine is a listed Hazardous Waste (RCRA and TRI) and a suspected Carcinogen (California P65)</p> <p>Strong Sulfuric Acid used in distillation.</p>	<p>Only dilute sulfuric acid and dilute sodium hydroxide used in the analysis method.</p> <p>Strong Sulfuric Acid used in distillation</p>
Data Analysis and Calculations	Continuous Flow Analyzer software performs calculations. Curves are linear, or second order.	Continuous Flow Analyzer software performs calculations. Curves are linear, or second order.
Method Validation Data	Interlaboratory precision and accuracy developed using 12 concentrations of CN spiked into a reagent water matrix.	<p>The determination step is based on ASTM D6888-04 and OIA 1677 and expected to have similar performance. ASTM D 2777 validation data presented in this report.</p> <p>Laboratory reagent water and a synthetic wastewater were spiked with <math>K_3Fe(CN)_6</math> and analyzed 7 times at three spike concentrations (20, 100, and 300 <math>\mu\text{g/L}</math> CN).</p> <p>Recovery ranged from 101 – 113 % and RSD were all less than 5%.</p> <p>Three real world samples (POTW effluent, creek water, and metals finishing water) were spiked with</p>

		$\text{K}_3\text{Fe}(\text{CN})_6$ at 100 $\mu\text{g/L}$ CN and analyzed 7 times. Recovery ranged from 87.1 – 97.3 % and RSD were all less than 5%.
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## Conclusion

ASTM D 7284-08 utilizes EPA approved distillation methods for total cyanide followed by measuring the available cyanide in the absorbing solution with flow injection, gas diffusion separation and amperometric detection, which is also based on EPA approved methods. ASTM D7284-08 is an acceptable alternative for the determination of total cyanide in environmental samples. The method has been validated by ASTM according to D 2777-06 and has been demonstrated to be more interference free than existing EPA approved methods.