

# Total Cyanide Determination by Segmented Flow Injection – On-line UV digestion with Amperometric Detection (OIA 1678)

## Introduction

In August 1997, OI Analytical contracted an independent consultant to evaluate problems associated with EPA approved distillation/colorimetric methods and compare them to a Segmented Flow Injection method utilizing ultraviolet irradiation to dissociate strong metal cyanide complexes and analyze the HCN produced by gas diffusion – amperometry. The study plan consisted of a comparison between the colorimetric and gas diffusion – amperometric determinative steps following distillation, a single lab validation of the on-line UV digestion method, and the preparation of spiked samples for a round robin analysis following USEPA ATP guidelines.

### Problems associated with EPA approved distillation methods

An obvious problem with distillation based cyanide methods is that they are time consuming with distillation apparatus occupying large amounts of bench space. A distillation by EPA method 335.4 requires a minimum of two hours and is usually performed on 10 place distillation blocks. Many laboratories utilize multiple blocks so that an entire QC batch can be distilled at once. The distillation process requires constant monitoring to maintain adequate flow rates and prevent hot digesting solution from overflowing into the distillation block. Results can vary widely between operators, between laboratories, and even day to day with a single operator. Bubbling rates and digestion temperatures can also have profound effects on interferences and recoveries.

Automated total cyanide methods utilizing ultraviolet irradiation followed by distillation and colorimetry have been also been developed. These methods can distinguish between total and simple cyanides simply by turning the UV irradiation off; distillation alone measures simple cyanides, and distillation combined with UV measures total cyanides<sup>1</sup>.

Most of the problems with interferences in total cyanide analysis by distillation result from the oxidizing, very low pH, boiling acid solution. The conditions in the flask, or in the flash distillation manifold of continuous flow analyzers, combined with complex sample matrices often react to produce cyanide when it is not present, or to destroy cyanide when it is actually there. In other words, the heat applied to distill cyanide generates results that, depending on sample matrices, may not be real.

In addition, there are positive interferences with the colorimetric tests from compounds that have reacted during the distillation and were captured in the absorber solution. More importantly, however, are the negative interferences produced by co distillates, such as sulfur dioxide, that compete in the color reaction preventing the detection of cyanide.

### Summary of the FIA UV digestion gas diffusion – amperometry method

The gas diffusion – amperometry method for determination of cyanide employs Flow Injection Analysis to “inject” an accurately measured aliquot of sample solution into a continuously flowing acidic stream. The cyanide in the sample reacts with the acid to form hydrogen cyanide gas that selectively diffuses through a micro porous, hydrophobic membrane into a basic carrier stream where it is detected by a very sensitive amperometric detector. One obvious advantage of FIA gas diffusion – amperometry is that CN ion is actually detected compared to colorimetric methods that determine cyanide indirectly after reaction with

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<sup>1</sup> Goulden, Peter D., Afghan, Badar K., Brooksbank, Peter, *Determination of Nanogram Quantities of Simple and Complex Cyanides in Water*, Anal. Chem. No. 11, Sept 1972, pp 1845 - 1849

chromogenic reagents. Other, significant advantages are the elimination of hazardous reagents, such as pyridine and barbituric acid, making the gas diffusion - amperometry method a “green chemistry”.

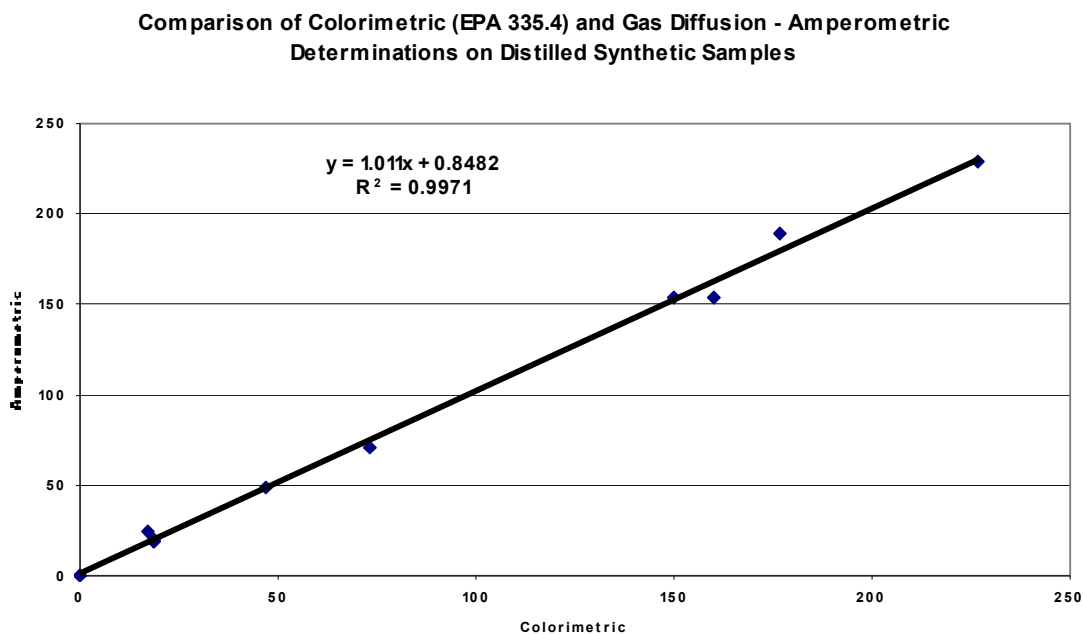
In acid solution ultraviolet irradiation liberates cyanide from strong metal complexes forming hydrogen cyanide. A narrow 312 nm irradiation wavelength limits side reactions and maximizes recovery from hard to digest ferric iron species. Once the sample leaves the digester it is further acidified and analyzed by gas diffusion – amperometry.

As mentioned above, in continuous flow methods, distillation alone only measures simple cyanide species. It is the UV irradiation that disassociates cyanide from the strong metal cyanide complexes. Using gas diffusion in place of distillation eliminates the need for heating the acidic solution and minimizes interferences.

### Comparison of FIA gas diffusion – amperometry with EPA 335.4 on distilled samples

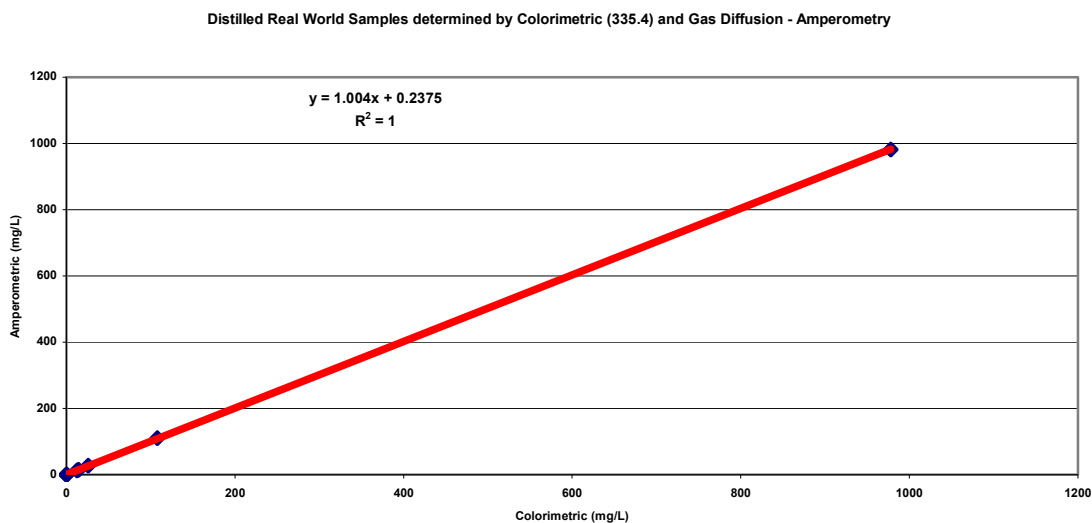
Synthetic, interference free samples (Figure 1) were prepared and distilled to demonstrate that gas diffusion – amperometry and colorimetric determinative steps generate the same result.

Figure 1



Once synthetic samples demonstrated equivalent results, several real world samples (Figure 2) were obtained, distilled, and the distillates analyzed by gas diffusion – amperometry and compared with colorimetry.

Figure 2



### Comparison of Segmented Flow Injection, UV Digestion, and Gas diffusion – amperometry with EPA 335.4 on distilled samples

Total distillations of 15 cyanide species were carried out in triplicate and compared to triplicate injections utilizing the new-segmented flow injection, UV digestion, and gas diffusion amperometry method. The data demonstrates that with few minor exceptions, and virtually no environmental significance, the two methods equally digest and detect essentially the same metallic cyanide species.

**Table 1** Species Dependent cyanide recoveries obtained with EPA 335.4 and OIA 1678 (ASTM D7511)

Species	0.200 mg/L CN		2.00 mg/L CN	
	EPA	FI-UV	EPA	FI-UV
[Zn(CN) <sub>4</sub> ] <sup>2-</sup>	99.5 (0.5) <sup>a</sup>	97.2 (1.8) <sup>a</sup>	104.4 (2.6) <sup>a</sup>	99.6 (1.9) <sup>a</sup>
[Cd(CN) <sub>4</sub> ] <sup>2-</sup>	103.8 (1.3)	104.3 (0.9)	102.9 (0.7)	100.9 (2.2)
[Cu(CN) <sub>4</sub> ] <sup>3-</sup>	97.7 (1.9)	100.0 (1.0)	98.0 (1.2)	100.3 (1.4)
[Ag(CN) <sub>2</sub> ] <sup>-</sup>	97.8 (2.3)	104.3 (1.2)	100.2 (2.6)	99.2 (0.4)
[Ni(CN) <sub>4</sub> ] <sup>2-</sup>	104.2 (3.5)	98.3 (2.5)	97.1 (0.3)	100.0 (0.4)
[Hg(CN) <sub>4</sub> ] <sup>2-</sup>	95.8 (2.5)	96.7 (2.3)	97.6 (3.3)	99.6 (2.4)
Hg(CN) <sub>2</sub>	98.0 (5.9)	96.1 (1.6)	97.3 ((0.9)	102.5 (0.8)
[Fe(CN) <sub>6</sub> ] <sup>4-</sup>	100.8 (5.5)	101.0 (0.5)	99.6 (2.0)	99.5 (1.0)
[Fe(CN) <sub>6</sub> ] <sup>3-</sup>	104.0 (1.3)	95.0 (1.6)	99.5 (2.8)	83.5 (1.8)
[Pd(CN) <sub>4</sub> ] <sup>2-</sup>	69.1 (2.5)	17.7 (2.6)	66.5 (1.9)	21.9 (1.6)
[Au(CN) <sub>2</sub> ] <sup>-</sup>	56.6 (2.0)	49.5 (1.3)	58.4 (1.9)	42.8 (1.0)
[Ru(CN) <sub>6</sub> ] <sup>4-</sup>	50.1 (1.7)	0.50 (1.9)	51.0 (1.1)	0.50 (2.0)
[Co(CN) <sub>6</sub> ] <sup>3-</sup>	ND <sup>b</sup>	13.8 (2.6)	2.5 (1.2)	14.6 (2.3)
[Pt(CN) <sub>4</sub> ] <sup>2-</sup>	ND	0.54 (2.3)	ND	0.44 (1.5)
[Pt(CN) <sub>6</sub> ] <sup>2-</sup>	ND	ND	ND	ND

<sup>a</sup> RSDs (%) (n = 3) are given in parenthesis. <sup>b</sup> Not Detected

To evaluate interferences, known interferences (at 20 and 200 mg/L levels) were distilled in triplicate together with 0.2 mg/L cyanide and analyzed by colorimetry.

**Table 2** EPA Method 335.4 determination of 0.200 mg/L CN (as NaCN) in the presence of possible interferences (20.0 or 200 mg/L)

Species	Ratio <sup>a</sup>	CN <sup>-</sup> found mg/L		Ratio <sup>a</sup>	CN <sup>-</sup> found mg/L	
		Untreated Samples	Treated Samples		Untreated samples	Treated Samples
NO <sub>2</sub> <sup>-</sup>	56	0.155 (3.4) <sup>b</sup>	0.203 (1.0)	560	0.133 (4.4)	0.204 (2.0)
SO <sub>3</sub> <sup>-</sup>	32	0.080 (10.0)		320	ND	
OCl <sup>-</sup>	50	ND <sup>c</sup>	0.120 (6.2)	500	ND	ND
CH <sub>3</sub> CHO	59	0.168 (6.0)	0.184 (4.8)	590	ND	0.028 (2.1)
SCN <sup>-</sup>	45	0.174 (8.0)		450	0.054 (1.0)	
S <sub>2</sub> O <sub>3</sub> <sup>-2</sup>	23	0.124 (4.3)		230	0.040 (3.2)	
S <sup>-2</sup>	81		0.120 (2.5) <sup>d</sup>	810		ND <sup>d</sup>

<sup>a</sup> Molar Concentration ratio: Species/CN<sup>-</sup>. <sup>b</sup> RSDs (%) (n = 3) are given in parenthesis. <sup>c</sup> Not Detected.

<sup>d</sup> Lead Carbonate addition and immediate (within 15 minutes) filtration.

Table 2 demonstrates significant interferences in the EPA approved distillation/colorimetric methods. These interferences also apply to automated methods that rely on distillation and utilize a colorimetric determinative step. In fact, automated colorimetric methods may be more susceptible to interference because they lack the operator intervention that may be required to detect sample specific interferences. To demonstrate that OIA 1678 performs equally, or better, than distillation/colorimetric methods 0.200 mg/l of cyanide (added as NaCN and iron cyanide complex) was analyzed in triplicate in the presence of potential interferences at concentrations 100 and 1000 times higher than the cyanide concentration. The data illustrates that, in the presence of certain interferences, OIA 1678 is superior to distillation/colorimetry.

**Table 3** OIA 1678 (ASTM D7511) determinations of 0.200 mg/L CN (added as [Fe(CN)<sub>6</sub>]<sup>-4</sup>) in the presence of possible interferences (20.0 or 200 mg/L)

Species	Ratio <sup>a</sup>	CN found mg/L		Ratio <sup>a</sup>	CN found mg/L	
		Untreated Samples	Treated Samples		Untreated Samples	Treated Samples
Cl <sup>-</sup>	73	0.197 (2.1) <sup>b</sup>		730	0.202 (1.7) <sup>b</sup>	
Br <sup>-</sup>	33	0.201 (2.3)		330	0.198 (0.8)	
I <sup>-</sup>	20	0.170 (1.2)		200	0.173 (1.2)	
SO <sub>4</sub> <sup>-2</sup>	27	0.194 (0.5)		270	0.197 (0.9)	
SO <sub>3</sub> <sup>-2</sup>	32	0.199 (1.3)		320	0.201 (0.3)	
NO <sub>3</sub> <sup>-</sup>	42	0.202 (2.3)		420	0.198 (2.8)	
NO <sub>2</sub> <sup>-</sup>	56	0.137 (0.7)	0.198 (0.8)	560	0.068 (4.2)	0.200 (0.5)
CO <sub>3</sub> <sup>-2</sup>	43	0.202 (0.6)		430	0.202 (0.5)	
OCN <sup>-</sup>	62	0.198 (1.6)		620	0.199 (2.6)	
OCl <sup>-</sup>	50	0.191 (0.6)	0.199 (1.5)	500	0.176 (1.7)	0.200 (0.9)
NH <sub>4</sub> <sup>+</sup>	144	0.200 (2.8)		1440	0.203 (0.9)	
CH <sub>3</sub> CHO	59	0.198 (1.8)	0.198 (1.3)	590	0.198 (2.2)	0.198 (1.7)
C <sub>3</sub> H <sub>8</sub> O <sub>3</sub>	28	0.199 (1.3)		280	0.199 (0.3)	
C <sub>6</sub> H <sub>12</sub> O <sub>6</sub>	14	0.200 (0.3)		140	0.196 (0.3)	
C <sub>6</sub> H <sub>8</sub> O <sub>6</sub>	15	0.198 (1.3)		150	0.196 (0.3)	
S <sup>-2</sup>	81	0.189 (0.8)	0.186 (1.1) <sup>c</sup>	810		0.148 (1.8) <sup>c</sup>
SCN <sup>-</sup>	45	0.199 (0.5)		450	0.204 (0.8)	
S <sub>2</sub> O <sub>3</sub> <sup>-2</sup>	23	0.197 (1.3)		230	0.199 (1.0)	

<sup>a</sup> Molar Concentration ratio: Species/CN<sup>-</sup>. <sup>b</sup> RSDs (%) (n = 3) are given in parenthesis. <sup>c</sup> Lead Carbonate addition and immediate (within 15 minutes) filtration.

**Table 5** OIA 1678 (ASTM D7511) determinations of 0.200 mg/L CN (added as NCN) in the presence of possible interferents (20.0 or 200 mg/L)

Species	Ratio <sup>a</sup>	CN found mg/L		Ratio <sup>a</sup>	CN found mg/L	
		Untreated Samples	Treated Samples		Untreated Samples	Treated Samples
Cl <sup>-</sup>	73	0.202 (1.4) <sup>b</sup>		730	0.201 (0.3) <sup>b</sup>	
Br <sup>-</sup>	33	0.198 (0.5)		330	0.197 (1.8)	
I <sup>-</sup>	20	0.204 (0.8)		200	0.203 (3.0)	
SO <sub>4</sub> <sup>-2</sup>	27	0.199 (1.3)		270	0.202 (1.2)	
SO <sub>3</sub> <sup>-2</sup>	32	0.199 (0.5)		320	0.175 (1.3)	
NO <sub>3</sub> <sup>-</sup>	42	0.201 (1.0)		420	0.201 (2.5)	
NO <sub>2</sub> <sup>-</sup>	56	0.199 (0.5)		560	0.199 (2.5)	
CO <sub>3</sub> <sup>-2</sup>	43	0.200 (1.6)		430	0.200 (0.5)	
OCN <sup>-</sup>	62	0.197 (1.3)		620	0.201 (1.2)	
OCl <sup>-</sup>	50	0.0	0.118 (3.0)	500	0.0	0.0
NH <sub>4</sub> <sup>+</sup>	144	0.202 (1.8)		1440	0.201 (1.2)	
CH <sub>3</sub> CHO	59	0.188 (2.0)	0.193 (1.2)	590	0.044 (1.3)	0.168 (2.1)
C <sub>3</sub> H <sub>8</sub> O <sub>3</sub>	28	0.199 (2.5)		280	0.200 (1.6)	
C <sub>6</sub> H <sub>12</sub> O <sub>6</sub>	14	0.202 (1.2)		140	0.185 (0.9)	
C <sub>6</sub> H <sub>8</sub> O <sub>6</sub>	15	0.199 (0.8)		150	0.188 (2.0)	
S <sup>-2</sup>	81	0.198 (1.0)		810		0.153 (1.3) <sup>c</sup>
SCN <sup>-</sup>	45	0.208 (1.4)		450	0.211 (2.4)	
S <sub>2</sub> O <sub>3</sub> <sup>-2</sup>	23	0.196 (1.1)		230	0.218 (2.9)	

<sup>a</sup>Molar Concentration ratio: Species/CN<sup>-</sup>. <sup>b</sup>RSDs (%) (n = 3) are given in parenthesis. <sup>c</sup>Lead Carbonate addition and immediate (within 15 minutes) filtration.

To further demonstrate method performance, nine real world samples were analyzed by OIA 1678 and compared to EPA Method 335.4.

**Table 6** Comparison of the cyanide values found by OIA 1678 (ASTM D7511) compared to EPA Method 335.4 for a series of real samples

Sample No.	CN <sup>-</sup> found mg/L	
	EPA 335.4	ASTM D????
1	978 (1.6) <sup>a</sup>	970 (0.5)
2	108.1 (2.1)	109.5 (0.9)
3	26.0 (1.6)	29.1 (0.7)
4	14.5 (2.3)	14.4 (1.0)
5	12.5 (1.4)	12.4 (1.0)
6	0.270 (2.6)	0.155 (1.0)
7	0.045 (13)	0.341 (0.4)
8	0.0258 (5.1)	0.0096 (2.8)
9	0.005 (3.5)	0.0050 (1.2)

<sup>a</sup> RSDs (%) (n = 3) are given in parentheses

## Characterization of interferences

### Thiocyanate

Thiocyanate alone presents a negative bias (see Table 2) upon analysis by all existing distillation cyanide methods, and a positive bias with OIA 1678. Acid concentrations and digestion times were investigated to determine the optimum time of UV exposure to obtain maximum recovery from ferric cyanide complexes while keeping recovery from thiocyanate at a minimum. Figure 3 is a plot comparing the generation of cyanide from three acid concentrations. The production of cyanide from thiocyanate, while not linear, is a function of the thiocyanate concentration in the sample. Figure 4 demonstrates the increase of ferric cyanide complex recovery as a function of irradiation time.

Figure 3

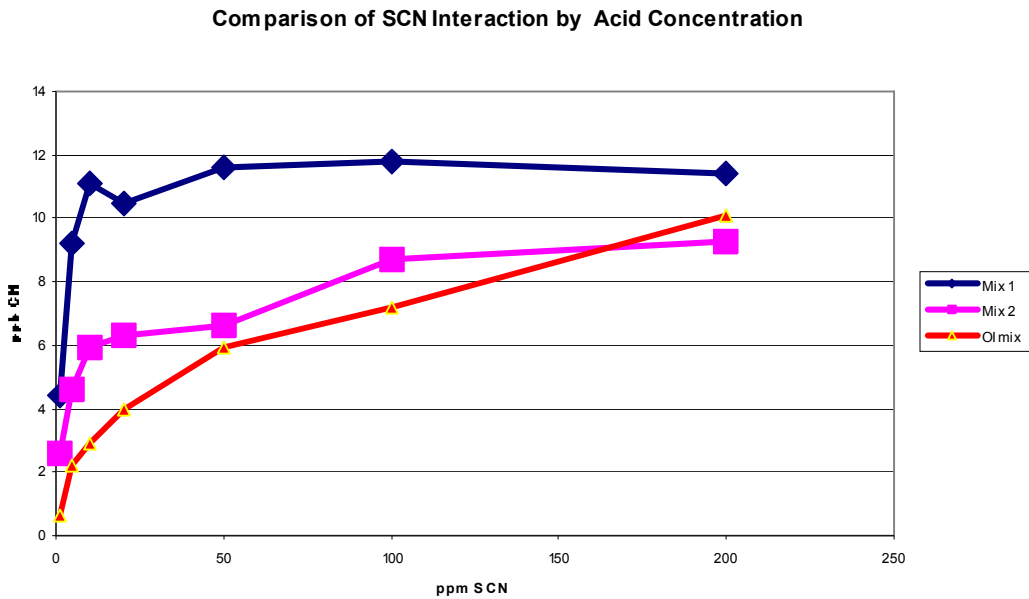
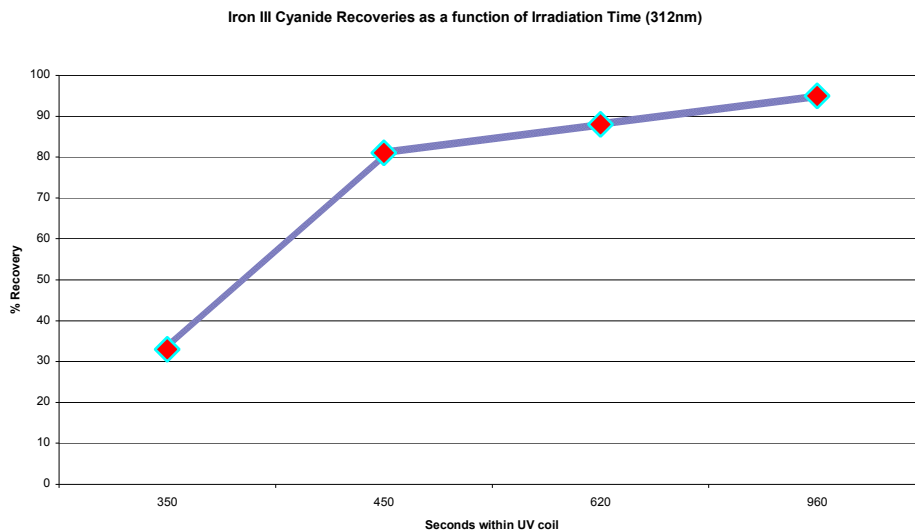


Figure 4



Thiocyanate in the presence of oxidizers, such as nitrate, results in significant positive bias in distillation based methods. 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 7). Thiocyanate and nitrate are both common contaminants in wastewater samples requiring cyanide analysis (Table 8). The nitrate concentration in wastewater effluents is typically 15 – 20 mg/L as NO<sub>3</sub>-N<sup>2</sup>. Also, since the “false” recoveries from thiocyanate plus nitrate are reproducible, spike recoveries cannot be used as an indicator for demonstrating the accuracy of a cyanide distillation (Table 9).

**Table 7** Thiocyanate Interference in Cyanide Analysis When Nitrate is Present in a Reagent Water Matrix<sup>3</sup>

Experiment #	SCN- (mg/L)	NO <sub>3</sub> - (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 8** 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

**Table 9** Comparison of Total Cyanide Results and Spike Recovery in a Synthetic Sample that does not contain cyanide <sup>a</sup>.

	SM 4500-CN C	EPA 335.3	ASTM D7284 - 08
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>.

<sup>2</sup> Metcalf and Eddy, Inc. 1991 *Wastewater Engineering: Treatment, Disposal, and Reuse*, 3<sup>rd</sup> Edition. McGraw-Hill, Inc., New York

<sup>3</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

OI Analytical, and ASTM D19.06 developed a “challenge” matrix containing 25 mg/L NO<sub>3</sub>-N and 15 mg/L SCN<sup>-</sup>. This “challenge” matrix should be used to evaluate all cyanide methods, and was used by OI Analytical to develop an alternative acidification reagent (TA1M) for OIA 1678 that eliminates false positives resulting from thiocyanate interferences. OI Analytical chemists using the TA1M reagent analyzed the “challenge” matrix and no significant interference (< 2 ppb CN). OI then contracted an independent laboratory to analyze their own preparation of this “challenge” matrix for total cyanide by OIA 1678 using the TA1M reagent. Independent laboratory results confirmed that the TA1M reagent exhibited no positive interference from thiocyanate and also quantitatively recovered total cyanide from a spiked “challenge” matrix.

### Thiosulfate and Sulfite

Low recoveries result from the analysis of samples containing thiosulfate and/or sulfite using distillation/colorimetric methods. This interference is a result of either evolution of H<sub>2</sub>S and entrapment in the basic absorber solution, or of SO<sub>2</sub> generation during distillation and subsequent absorption as SO<sub>3</sub><sup>-2</sup> (sulfite) in the absorber solution. Sulfite is listed as an interferent in most colorimetric methods including SM4500, ASTM D2036, ISO 14403, and Kelada 01. Since sulfite interferes by increasing chlorine demand, negative bias due to its presence will likely go undetected by automated colorimetric methods. OIA 1678 quantitatively recovers CN<sup>-</sup> in sample containing sulfite and thiosulfate (see Table 5).

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>4</sup>. Sulfite is also used extensively as a dechlorination agent for treating wastewater disinfected by chlorination<sup>5</sup>. In other words, sulfite is a likely constituent of water samples slated for cyanide analysis. Distillation based colorimetric methods do not quantitatively recover cyanide in the presence of sulfite (see Table 2).

The reaction products of thiosulfate in strong acid solution (distillations) 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, and distills into the absorber solution and converts to sulfite. Sulfite interferences are listed above. Therefore, thiosulfate interferes with colorimetric cyanide determinations in a manner similar to sulfite. ASTM D2036 mentions sulfur oxides as a potential interference without specifically naming thiosulfate. Kelada – 01, a UV digestion – online distillation – colorimetric cyanide method, mentions that both thiosulfate and sulfite were evaluated for oxidant removal and found to interfere with the method.

### Sulfide

Sulfide is listed as an interferent in all cyanide 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 complex resulting in low recoveries. Lead carbonate (SM4500 and ASTM D2036) reacts with sulfide to form lead sulfide. The lead sulfide reacts rapidly converting cyanide to thiocyanate within minutes<sup>6</sup>. Other precipitation methods such as the use of bismuth (SW846 9010C), and sulfide removal based on selective volatilization of H<sub>2</sub>S (40 CFR part 136 Table II footnotes) are also ineffective. Table 10 lists some sulfide removal (200 mg/L S<sup>-2</sup>) procedures and

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<sup>4</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>5</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

<sup>6</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)

typical recoveries for total cyanide. OIA 1678 reagent TA2 contains the same sulfide removal procedures as ASTM D 7284 – 08 and ASTM D6888-04. The reagent removes sulfide prior to gas diffusion preventing it from interfering with cyanide detection. Figure 5 illustrates that the sulfide abatement reagent (TA2) successfully overcomes sulfide interference at concentrations up to 50 mg/L S<sup>-2</sup>.

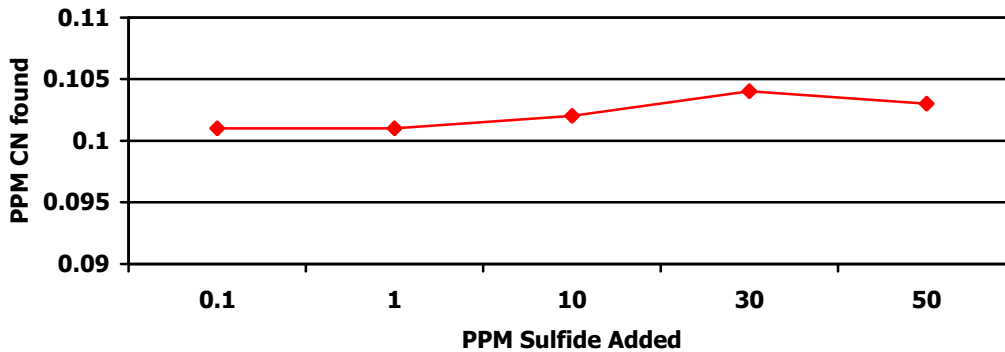
**Table 10** Total Cyanide Recovery after removal of 200 mg/L S<sup>-2</sup> by various procedures <sup>a</sup>. Analysis by ASTM D 7284-08 / D 6888-04

Sulfide Removal Method	Recovery
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.

**Figure 5** Plot of Cyanide recoveries in the presence of Sulfide by FIA gas diffusion amperometry and sulfide abatement reagents



### Single Laboratory Validation

Nine representative matrices were identified along with eight laboratories for participation in a round robin validation of OIA 1678 as an application for nationwide use of the method as an Alternative Test Procedure (ATP). Prior to the round robin, the samples were characterized at the University of Nevada in Reno. Each sample was analyzed and spiked in triplicate. Spikes were prepared using various cyanide species and at levels to encompass the analytical range of the method.

**Table 11.** Results of OIA 1678 (ASTM D7511) determination of cyanide in various industrial samples (single lab study)

Sample	CN <sup>-</sup> found in the original sample mg/L	Type and concentration of spike mg/L	CN <sup>-</sup> found in the spiked sample mg/L	Spike Recovery (%)
Drum handling facility (filter effluent)	0.045 (2.0) <sup>a</sup>	2.00 as [Fe(CN) <sub>6</sub> ] <sup>-4</sup>	2.060 (1.2)	101
POTW (secondary effluent)	0.004 (1.2)	0.10 as [Fe(CN) <sub>6</sub> ] <sup>-3</sup>	0.100 (0.3)	96
Petroleum refinery (secondary effluent)	0.380 (1.9)	2.00 as [Ag(CN) <sub>2</sub> ] <sup>-</sup> + 2.00 as [Ni(CN) <sub>4</sub> ] <sup>-2</sup>	4.40 (1.8)	101
Coke plant (secondary effluent)	3.45 (2.1)	1.00 as [Hg(CN) <sub>4</sub> ] <sup>-2</sup>	4.47 (1.1)	102
Rolling mill (secondary effluent)	ND <sup>b</sup>	0.020 as [Fe(CN) <sub>6</sub> ] <sup>-4</sup>	0.020 (1.1)	100
Metals forming plant (primary effluent)	0.004 (3.6)	0.010 as [Fe(CN) <sub>6</sub> ] <sup>-3</sup>	0.0145 (2.2)	105
Die casting plant (secondary effluent)	0.030 (1.1)	0.020 as [Fe(CN) <sub>6</sub> ] <sup>-4</sup>	0.052 (2.8)	110
Precious metal operation (reclaim water)	0.033 (2.1)	1.00 as [Fe(CN) <sub>6</sub> ] <sup>-4</sup> + 20.0 SCN <sup>-</sup>	1.030 (1.3)	99.7
Water treatment plant (filter effluent)	0.007 (3.2)	0.010 as CN <sup>-</sup>	0.0165 (1.4)	95.0

<sup>a</sup> RSDs (%) (n = 3) are given in parentheses.

Once adequately characterized by the single laboratory study, the same samples were prepared, packaged and shipped to the participating laboratories and identified only by sample number (sample #).

Table 12. Identification of samples prepared for Round Robin OIA 1678 (ASTM D7511)

Sample	Sample #	Type and concentration of spike mg/L	Expected CN mg/L
Drum handling facility (filter effluent)	30751	2.00 as $[\text{Fe}(\text{CN})_6]^{-4}$	2.04
POTW (secondary effluent)	30752	0.10 as $[\text{Fe}(\text{CN})_6]^{-3}$	0.100
Petroleum refinery (secondary effluent)	30753	2.00 as $[\text{Ag}(\text{CN})_2]^{-}$ + 2.00 as $[\text{Ni}(\text{CN})_4]^{-2}$	4.32
Coke plant (secondary effluent)	30754	1.00 as $[\text{Hg}(\text{CN})_4]^{-2}$	3.45
Rolling mill (secondary effluent)	30755	0.020 as $[\text{Fe}(\text{CN})_6]^{-4}$	0.020
Metals forming plant (primary effluent)	30756	No spike	0.004
Die casting plant (secondary effluent)	30757	No spike	0.030
Precious metal operation (reclaim water)	30758	1.00 as $[\text{Fe}(\text{CN})_6]^{-4}$ + 20.0 $\text{SCN}^{-}$	1.030
Water treatment plant (filter effluent)	30759	No spike	0.007

Table 13 Identification of laboratories for OIA 1678 (ASTM D7511) Round Robin Testing

University of Nevada at Reno  
 Delta Faucet, Greensburg Indiana  
 University of North Carolina at Chapel Hill  
 INTEL  
 Bayer Material Science  
 American Scientific Laboratories (ASL)  
 Alpkem  
 Golden Sunlight Mine

## Round Robin Testing Laboratory Results

Presented in no particular order.

	mean	inj. 1	inj. 2	inj. 3
MDL (ug/l)	0.63			
ML (ug/l)	2.0034			
IPR (50 ug CN/L as Ferrous CN complex)	49.0	47.9	49.5	49.3
IPR (50 ug CN/L as Ferrous CN complex)	47.4	47.8	46.4	48
IPR (50 ug CN/L as Ferrous CN complex)	48.5	50.6	47.5	47.4
IPR (50 ug CN/L as Ferrous CN complex)	48.1	47.2	48.4	48.8
CCV (50 ug/L CN as NaCN)	53.0	52.5	51.9	54.6
Blank	0.0	0	0	0
30756	4.4	4	4.5	4.7
30759	6.5	6.8	6.2	6.4
30755	20.8	21.6	20.4	20.5
30757*	27.6	29.3	25.6	28
CCV (50 ug/L CN as NaCN)	52.6	53.3	52.6	51.9
30752	99	99.3	101.1	98
LCS (50 ug/L CN as Ferric CN complex)	53.6	55.8	53	52.1
LMS I (50 ug/L CN as Ferric CN complex)	42.3	44.3	41.3	41.2
LMS II (50 ug/L CN as Ferric CN complex)	43.3	45.7	41.7	42.4
CCV (50 ug/L CN as NaCN)	53.3	53.1	51.2	55.5
30758	1083	1080	1070	1100
30751	2070	1990	2090	2130
30754	3390	3480	3340	3350
30753	4403	4370	4460	4380
CCV (2000 ug/L CN as NaCN)	2063	2110	2060	2020
LCS (2000 ug/L CN as Ferric CN complex)	1987	2100	1960	1900

	mean	inj. 1	inj. 2	inj. 3
MDL (ug/l)	0.19			
ML (ug/l)	0.6			
IPR (50 ug CN/L as Ferrous CN complex)	47.5	46.1	50.6	45.7
IPR (50 ug CN/L as Ferrous CN complex)	49.3	47.4	50.8	49.7
IPR (50 ug CN/L as Ferrous CN complex)	48.7	50	46.5	49.6
IPR (50 ug CN/L as Ferrous CN complex)	47.4	47.2	48.7	46.4
CCV (50 ug/L CN as NaCN)	50.0	51.2	48.5	50.4
Blank	-1.0	-1.11	-0.6	-1.4
30756	7.1	7.6	6.42	7.41
30759	12.0	12.1	11.9	11.9
30755	25.2	24	25	26.5
30757*	246.3	244	249	246
CCV (50 ug/L CN as NaCN)	48.7	49	47.7	49.5
30752	78	79.6	76	77.5
LCS (50 ug/L CN as Ferric CN complex)	48.0	47.5	48.4	48.2
LMS I (50 ug/L CN as Ferric CN complex)	39.9	40.7	41.4	37.5
LMS II (50 ug/L CN as Ferric CN complex)	39.6	39.6	40.4	38.7
CCV (50 ug/L CN as NaCN)	50.8	51.7	50.6	50.1
30758				
30751				
30754				
30753				
CCV (2000 ug/L CN as NaCN)				
LCS (2000 ug/L CN as Ferric CN complex)				

	Mean	inj. 1	inj. 2	inj. 3
MDL (ug/l)	0.414			
ML (ug/l)	1.3			
IPR (50 ug CN/L as Ferrous CN complex)	49.0	48	51	49
IPR (50 ug CN/L as Ferrous CN complex)	46.3	47	44	48
IPR (50 ug CN/L as Ferrous CN complex)	46.0	44	47	47
IPR (50 ug CN/L as Ferrous CN complex)	49.3	53	48	47
CCV (50 ug/L CN as NaCN)	47.0	50.4	43.4	47.3
Blank	0.4	0.8	0.2	0.2
30756	8.6	9.3	8.1	8.5
30759	8.3	8.9	7.7	7.7
30755	6.8	6.7	7	6.7
30757*	25.7	28.9	20.6	27.6
CCV (50 ug/L CN as NaCN)	51.3	52.5	49.8	51.5
30752				
LCS (50 ug/L CN as Ferric CN complex)	51.6	52.8	49.5	52.6
LMS I (50 ug/L CN as Ferric CN complex)	21.6	23.6	21.4	19.8
LMS II (50 ug/L CN as Ferric CN complex)	23.9	24.3	22	25.5
CCV (50 ug/L CN as NaCN)	50.0	49.9	48.9	51.2
30758	913.3	864	995	881
30751	2009	2002	1934	2091
30754	2354	2245	2331	2486
30753	4078	4066	3850	4319
CCV (2000 ug/L CN as NaCN)	2177	2142	2331	2059
LCS (2000 ug/L CN as Ferric CN complex)	1938	1984	1841	1990

	Mean	inj. 1	inj. 2	inj. 3
MDL (ug/l)	1.76			
ML (ug/l)	5.6			
IPR (50 ug CN/L as Ferrous CN complex)	45.2	44.8	45.5	45.2
IPR (50 ug CN/L as Ferrous CN complex)	44.1	43.2	45.9	43.3
IPR (50 ug CN/L as Ferrous CN complex)	43.4	44.6	43.2	42.5
IPR (50 ug CN/L as Ferrous CN complex)	41.7	41.6	41	42.4
CCV (50 ug/L CN as NaCN)	52.3	50.4	53.2	53.3
Blank	0.0	0	0	0
30756	5.5	5.94	5.51	5.02
30759	11.8	12	12.3	11.2
30755	21.8	21.8	21.9	21.6
30757*	41.5	41.7	40.8	42.1
CCV (50 ug/L CN as NaCN)	59.3	61.6	59.6	56.6
30752	102	101	104	102
LCS (50 ug/L CN as Ferric CN complex)	44.8	45.3	45.2	43.9
LMS I (50 ug/L CN as Ferric CN complex)	41.1	41.2	41.4	40.7
LMS II (50 ug/L CN as Ferric CN complex)	41.2	40.9	41.3	41.5
CCV (50 ug/L CN as NaCN)	56.1	56	55.8	56.6
30758	762.3	763	764	760
30751	1496	1558	1460	1469
30754	1709	1761	1685	1680
30753	3372	3416	3402	3298
CCV (2000 ug/L CN as NaCN)	1440	1459	1434	1426
LCS (2000 ug/L CN as Ferric CN complex)	1091	1086	1100	1088

	Mean	inj. 1	inj. 2	inj. 3
MDL (ug/l)	0.543			
ML (ug/l)	1.73			
IPR (50 ug CN/L as Ferrous CN complex)	48.5	49.1	47.9	48.4
IPR (50 ug CN/L as Ferrous CN complex)	48.2	48.2	47.8	48.6
IPR (50 ug CN/L as Ferrous CN complex)	47.7	48.5	47.8	46.7
IPR (50 ug CN/L as Ferrous CN complex)	46.9	46.9	46.3	47.6
CCV (50 ug/L CN as NaCN)	49.4	51.2	48.6	48.3
Blank	0.0077	0	0.023	0
30756	6.00	6.76	5.6	5.64
30759	4.95	5.16	4.77	4.92
30755	19.8	19.2	21.1	19.2
30757*	20.1	21.2	20.4	18.8
CCV (50 ug/L CN as NaCN)	50.0	49.2	50.7	50
30752	101.1	103	101	99.4
LCS (50 ug/L CN as Ferric CN complex)	48.9	47.2	47.6	51.9
LMS I (50 ug/L CN as Ferric CN complex)	39.4	40	38.6	39.7
LMS II (50 ug/L CN as Ferric CN complex)	39.0	38.6	39.1	39.2
CCV (50 ug/L CN as NaCN)	48.8	48.6	48.5	49.4
30758	1047	1050	1050	1040
30751	1787	1770	1790	1800
30754	2533	2570	2540	2490
30753	3853	3890	3830	3840
CCV (2000 ug/L CN as NaCN)	1810	1840	1790	1800
LCS (2000 ug/L CN as Ferric CN complex)	1530	1580	1520	1490

	Mean	inj. 1	inj. 2	inj. 3
MDL (ug/l)	3.2			
ML (ug/l)	10.1			
IPR (50 ug CN/L as Ferrous CN complex)	46.0	47.7	44.3	46
IPR (50 ug CN/L as Ferrous CN complex)	53.2	49.5	56.9	53.2
IPR (50 ug CN/L as Ferrous CN complex)	44.4	48.8	40.1	44.4
IPR (50 ug CN/L as Ferrous CN complex)	46.1	45.8	45.6	46.9
CCV (50 ug/L CN as NaCN)	46.3	44	44	51
Blank	1.5667	3	0.9	0.8
30756	5.33	6	5	5
30759	11.33	11	12	11
30755	20.0	20	20	20
30757*	67.0	71	65	65
CCV (50 ug/L CN as NaCN)	45.3	45	46	45
30752	73.3	75	73	72
LCS (50 ug/L CN as Ferric CN complex)	40.3	37	43	41
LMS I (50 ug/L CN as Ferric CN complex)	43.0	42	44	43
LMS II (50 ug/L CN as Ferric CN complex)	43.7	43	48	40
CCV (50 ug/L CN as NaCN)	51.0	52	50	51
30758	1107	1120	1060	1140
30751	2123	2140	2100	2130
30754	3617	3640	3720	3490
30753	4747	4820	4720	4700
CCV (2000 ug/L CN as NaCN)	1880	1880	1690	2070
LCS (2000 ug/L CN as Ferric CN complex)	1907	1760	2030	1930

	Mean	inj. 1	inj. 2	inj. 3
MDL (ug/l)	0.27			
ML (ug/l)	0.86			
IPR (50 ug CN/L as Ferrous CN complex)	42.5	41.4	42.8	43.3
IPR (50 ug CN/L as Ferrous CN complex)	50.8	52.9	49.5	50
IPR (50 ug CN/L as Ferrous CN complex)	50.3	50.2	50.2	50.6
IPR (50 ug CN/L as Ferrous CN complex)	50.2	52.9	48.9	48.7
CCV (50 ug/L CN as NaCN)	52.8	53.2	52.4	52.7
Blank	-1.4000	-1.4	-1.4	-1.4
30756	5.57	5.1	6.1	5.5
30759	7.90	7.6	8	8.1
30755	21.8	21.7	21.6	22
30757*	32.0	32.6	31.5	31.9
CCV (50 ug/L CN as NaCN)	52.1	52.6	51.2	52.4
30752	98.9	98.4	99.8	98.4
LCS (50 ug/L CN as Ferric CN complex)	50.1	49.3	48.6	52.4
LMS I (50 ug/L CN as Ferric CN complex)	44.1	43.6	44.2	44.5
LMS II (50 ug/L CN as Ferric CN complex)	44.1	43.6	44.2	44.5
CCV (50 ug/L CN as NaCN)	42.8	42	43	43.4
30758	1071	1048	1065	1099
30751	1864	1805	1952	1835
30754	3304	3267	3327	3319
30753	4140	4075	4131	4214
CCV (2000 ug/L CN as NaCN)	2007	1951	2072	1999
LCS (2000 ug/L CN as Ferric CN complex)	1913	1902	1947	1890

	Mean	inj. 1	inj. 2	inj. 3
MDL (ug/l)	0.4			
ML (ug/l)	1			
IPR (50 ug CN/L as Ferrous CN complex)	51.7	51.1	52.5	51.5
IPR (50 ug CN/L as Ferrous CN complex)	52.2	52.6	52.1	51.9
IPR (50 ug CN/L as Ferrous CN complex)	55.6	52.6	53.1	61.1
IPR (50 ug CN/L as Ferrous CN complex)	54.7	55.1	54.7	54.2
CCV (50 ug/L CN as NaCN)	46.9	46.7	47.1	46.9
Blank	0.0000	0	0	0
30756	6.56	6.93	6.5	6.26
30759	6.11	6.01	6.61	5.72
30755	20.3	18.6	20.6	21.8
30757*	8.7	6.04	8.18	12
CCV (50 ug/L CN as NaCN)	48.3	48.9	49.9	46
30752	102.7	103	104	101
LCS (50 ug/L CN as Ferric CN complex)	50.2	52.8	49.2	48.7
LMS I (50 ug/L CN as Ferric CN complex)	45.0	44	46.3	44.6
LMS II (50 ug/L CN as Ferric CN complex)	52.7	50	58	50
CCV (50 ug/L CN as NaCN)	57.6	59	49.6	64.3
30758	831	828	840	826
30751	1571	1522	1574	1618
30754	2289	2328	2234	2306
30753	4242	4218	4293	4216
CCV (2000 ug/L CN as NaCN)	1865	1842	1852	1900
LCS (2000 ug/L CN as Ferric CN complex)	1358	1338	1371	1364

Table 14. Summary of Useable Data, averages of triplicate analyses

Concentration (ug/L)									
Lab ID	30756	30759	30755	30757*	30752	30758	30751	30754	30753
	4.0	7.0	20.0	30.0	100	1030	2040	3450	4320
1	4.4	6.5	20.8	27.6	99.0	1083	2070	3390	4403
2	7.1	12.0	25.2	R	78	N	N	N	N
3	8.6	8.3	6.8	25.7	N	913	2009	2354	4078
4	5.5	11.8	21.8	41.5	102	762	1496	1709	3372
5	6.0	4.95	19.8	20.1	101	1047	1787	2533	3853
6	5.33	11.3	20.0	67.0	73.3	1107	2123	3617	4747
7	5.57	7.90	21.8	32	98.9	1071	1864	3304	4140
8	6.56	6.11	20.3	8.7	103	831	1571	2289	4242

R = Data (246 ug/L) rejected as outlier

N = No data submitted

\* = Sample is colloidal, making representative sampling difficult

Table 15. Final Statistical Summary

Sample	30756	30759	30755	30757	30758	30758	30751	30754	30753
No. Values	24	24	24	21	21	21	21	21	21
True value ug/L	4.0	7.0	20.0	30.0	100	1030	2040	3450	4320
Mean	6.1	8.6	19.6	31.8	93.6	974	1850	2740	4320
% Recovery	153	123	97.8	107	93.6	94.5	90.5	79.5	95.4
Overall Std Dev	1.29	2.77	5.43	18.5	12.5	137	243	703	432
Overall % RSD	21	32	28	58	13	14	13	26	11

Table 16. Quality Control Acceptance Criteria

Parameter	Value (ug/L)	% Recovery	Precision
MDL	1.0		
ML	3.0		
IPR (as Fe II CN)	50.0	82 - 118	≤ 12% RSD
OPR (as Fe II CN)	50.0	84 - 116	NA
OPR (as Fe II CN)	2000	71 - 128	NA
MS/MSD (as Fe III CN)	50.0	64 - 136	≤ 47% RPD
CCV (as KCN or NaCN)	50.0	90 - 110	≤ 10 % RPD
CCV (as KCN or NaCN)	2000	85 - 115	≤ 15 % RPD

### Peer reviewed Articles and Data

There have been numerous peer reviewed and journal articles that have evaluated OIA 1678 for the analysis of total cyanide in environmental samples.

Berman R., Christmann D., and Renn C., *Automated Determination of weak acid dissociable and total cyanide without thiocyanate interference*, American Environmental Laboratory, June 1993

Solujic L., Milosavljevic E.B., and Straka M.R., *Total cyanide determination by a segmented flow injection-on-line UV digestion amperometric method*, The Analyst 1999, 124, 1255 – 1260

Weinberg H.S., and Cook S.J., *Segmented Flow Injection, UV Digestion, and Amperometric Detection for the Determination of Total Cyanide in Wastewater Treatment Plant Effluents*, Anal. Chem. 2002, 74, 6055 – 6063

Berman R., and Martin T.H., *Avoiding Cyanide Compliance Problems*, 15<sup>th</sup> AESF/EPA Pollution Prevention & Control Conference, January 24 – 27, 1994

Docket No. W-98-08, UWSAG response to method OIA 1677, Appendix A, *Comparison of Cyanide Analysis Methods*, September 4, 1998

Users of total cyanide systems have made numerous unpublished comparisons available to OI. The following graph plots over 50 real world electroplating sample analyses comparing method 1678 to both automated UV digestion – inline distillation – colorimetric (Figure 6) and manual (Figure 7) distillation methods.

Figure 6.

Comparison of OIA 1678 (Proposed ASTM Non-Distillation method) with EPA 335.3 Automated UV - Distillation Colorimetry) on Real Samples

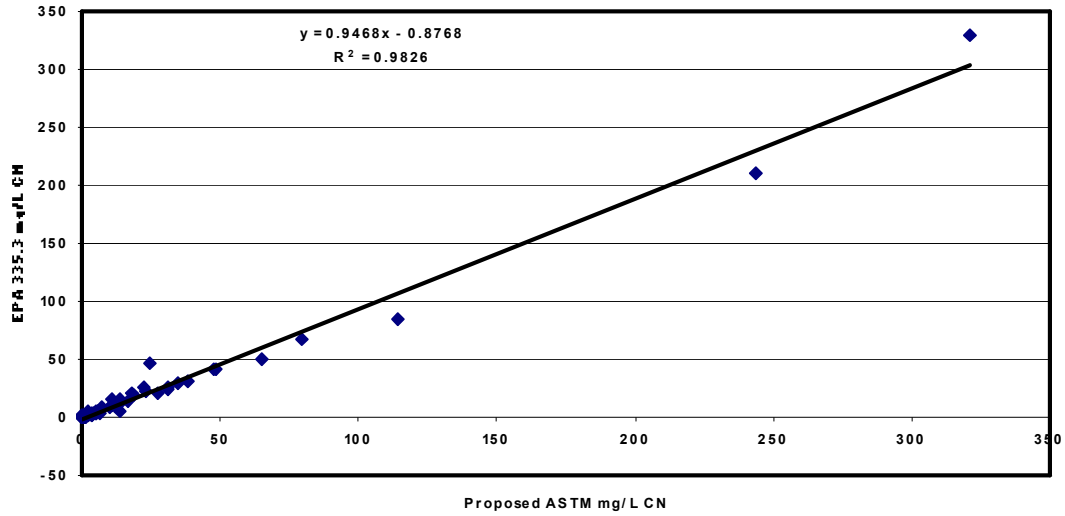
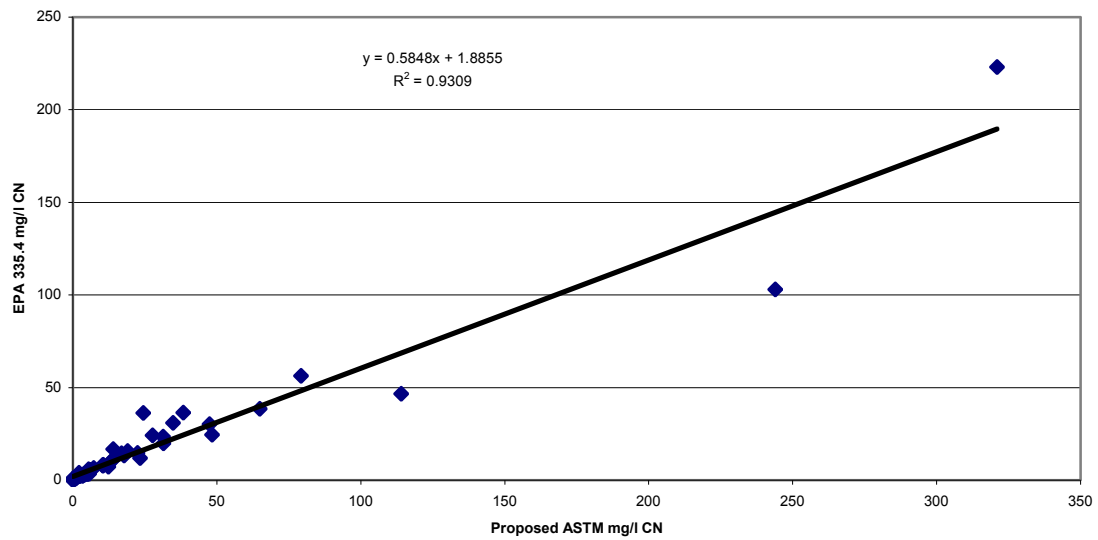


Figure 7

Comparison of OIA 1678 (Proposed ASTM Non Distillation Method) with EPA 335.4 (manual distillation followed by automated colorimetry) on Real samples



## **Conclusion**

The FIA method, OIA 1678, proposed to ASTM for the analysis of total cyanide by UV digestion utilizing a gas diffusion – amperometric determinative step provides potential users with a rapid, cost effective alternative to distillation based cyanide methods. UV irradiation without distillation has been demonstrated less prone to interferences and uses less toxic reagents. In addition, this method overcomes many deficiencies in distillation/colorimetric methods that result in poor precision and extreme positive or negative bias. The method has been extensively researched and numerous peer-reviewed articles validating the method have been published.