Frontiers in Automated Analysis of Cyanide

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Abstract

Flow injection analysis (FIA) with gas diffusion separation and amperometric detection has been demonstrated to be the most effective way for automating the chemical analysis of cyanide. In 1999, the USEPA approved Method OIA-1677 for NPDES monitoring of available cyanide using ligand displacement and flow injection analysis with amperometric detection as an alternative to the problematic cyanide-amenable-to-chlorination (CATC) procedure. Using similar technology, ASTM Committee D19 on Water developed ASTM Standard Test Method D6888. ASTM Committee D19 has also developed a new method to measure aquatic free cyanide and is currently working on amperometric methods for determination of total cyanide using UV digestion or manual distillation to dissociate the cyanide metal complexes. ASTM Committee D22 on Air Quality is currently reviewing new methodology for determination of hydrogen cyanide in air and combustion products.

This poster highlights methods using current technology and summarizes improvements in flow injection analysis with amperometric detection using the CNSolution FS 3100 from OI Analytical. The results for sample evaluation are reviewed. The advantages of using new methods employing flow injection analysis with amperometric detection for cyanide analysis are also discussed.

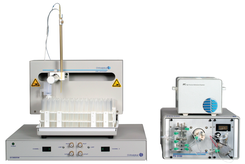

Figure 1. OI Analytical CNSolution FS 3100 flow injection analysis system with amperometric detection

Table 1. Cyanide analysis by flow injection analysis (FIA) with gas diffusion separation and amperometric detection using the CNSolution FS 3100 system

Cyanide Species	Method	Method Status
Available cyanide	USEPA OIA-1677 ASTM D6888-04	Approved
Aquatic free cyanide	ASTM D7237	Approved; currently being edited by ASTM editors for publication.
Hydrogen cyanide present or generated during fires	Guide E800	A draft standard is currently under review by ASTM Committee D22 on Air Quality. ASTM Committee E5 on Fire Standards is considering adding the procedure to Guide E800.
Total cyanide	TBD	Standards are currently in development by ASTM Committee D19 on Water.

Available Cyanide

Approximately 200 samples (consisting of calibration standards, effluent samples, MS/MSDs, and quality controls) were analyzed for available cyanide as described in USEPA Method OIA-1677 and ASTM D6888-04. All samples were analyzed with TEP and dithizone as the ligand exchange reagents, which are described in the ASTM standard. Initial precision and recovery samples were analyzed, and the method detection limit (MDL) was determined by injecting a 2 µg/L standard seven times.

All quality control criteria from USEPA Method OIA-1677 and ASTM D6888-04 were met using the FS 3100 system including calibration checks, laboratory control samples, method blanks, etc. The observed method detection limit was 0.45 µg/L CN^-, and the mean recovery of the initial precision and recovery samples was 97.0% (0.73 % RSD). The data for the initial demonstration of proficiency are shown in Tables 2 and 3. Accuracy at 2 µg/L CN^-can be improved by narrowing the calibration standard range from 2 to 200 µg/L CN^-. Using a second order fit for the calibration curve is also recommended. Typically, the reporting limit for available cyanide is 2 µg/L CN^-, which is the USEPA minimum level (ML).

Table 2. Available cyanide demonstration of proficiency

Sample	Spike Concentration, µg/L	Concentration Found, µg/L
IPR 1	200	195
IPR 2	200	194
IPR 3	200	192
IPR 4	200	195
% Mean Recovery	*97.0*	
% RSD	*0.73*	

IPRs prepared with $Hg(CN)_2$ as described in USEPA OIA-1677.

Table 3. Available cyanide method detection limit

Sample	True Value, µg/L	Concentration Found, µg/L
MDL 1	2.00	1.09
MDL 2	2.00	1.16
MDL 3	2.00	1.32
MDL 4	2.00	1.40
MDL 5	2.00	1.48
MDL 6	2.00	1.41
MDL 7	2.00	1.37
Standard Deviation	*0.142*	
Observed MDL, µg/L	*0.446*	
USEPA Method ML, µg/L	*2.00*	

Aquatic Free Cyanide

A new method to measure aquatic free cyanide (HCN and dissociated CN^- present at the pH of receiving water) was recently developed by ASTM Committee D19 on Water. The method does not require ligand exchange reagents and uses a buffered acidification reagent at pH 6, pH 7, or pH 8. This method was validated with an interlaboratory study consisting of nine laboratories. The round robin data were evaluated for precision and bias according to ASTM D7237.

Since ASTM D7237 requires a reproducible sample matrix, synthetic precious metals wastewater was prepared with known cyanide concentrations in the presence of several potential interferences including 25 mg/L NH_3 as N, 15 mg/L SCN, 25 mg/L OCN, and 25 mg/L NO_3. The certified solutions were prepared by High Purity Standards (Charleston, SC). The Bayer MaterialScience Environmental Analytics laboratory divided the samples for distribution to laboratory participants, who did not know the certified values at the time of the study. Tables 4 and 5 show the intralaboratory data and the Bayer laboratory's results obtained with the FS 3100 system.

Table 4. Aquatic free cyanide interlaboratory statistical summary

Sample	Mean µg/L	% RSD	True Value µg/L	% Mean Recovery
Calibration check	196	5.81	200	98.1
SPEX QC-CN-WS	202	8.84	204	98.9
Method blank	–0.241	—	0	—
Calculated MDL = Std. Dev. x 3.14	0.470	62.4	—	—
Calibration check	196	8.89	200	98.0
SPEX QC-CN-WS	197	10.9	204	96.4
Method blank	–0.440	—	0	—
Sample 1	0.816	—	0	—
Sample 2	409	13.3	400	102
Sample 3	352	12.1	350	100
Sample 4	134	7.55	130	103
Sample 5	7.00	31.3	6	117
Sample 6	5.66	21.4	5	113
Sample 7	116	6.73	110	106
Calibration check	195	9.07	200	97.4
SPEXS QC-CN-WS	198	12.7	204	97.0
Method blank	–0.342	—	0	—

This table is based on data from eight reporting laboratories. Data from a ninth laboratory was not included due to instrument issues.

Table 5. Aquatic free cyanide, ASTM interlaboratory study conducted with the FS 3100 system

Sample	Concentration (µg/L)	Instrument Response (pA)	Observed Result Aquatic Free Cyanide (µg/L)
Calibration Standards (Prepared in Section 8.8)			
Calibration standard 1	0	–106	0.209
Calibration standard 2	2	2,478	1.60
Calibration standard 3	5	9,985	5.66
Calibration standard 4	10	17,481	9.72
Calibration standard 5	20	37,213	20.5
Calibration standard 6	50	85,234	47.0
Calibration standard 7	100	185,437	104
Calibration standard 8	200	343,162	198
Calibration standard 9	500	797,777	500
Calibration Check, QC-CN-WS, and Laboratory Method Blank (Sections 16.2, 16.4, 16.5)			
Calibration check	200	325,602	187
SPEX QC-CN-WS	204	349,260	202
Method blank	—	153	0.349
The provided QC-CN-WS acceptance range is 153 to 255 µg/L CN.			
Method Detection Limit Determination (Inject 2 µg/L Standard Seven Times)			
MDL 1	2	3,651	2.24
MDL 2	2	3,783	2.31
MDL 3	2	3,543	2.18
MDL 4	2	4,366	2.62
MDL 5	2	3,609	2.21
MDL 6	2	3,717	2.27
MDL 7	2	3,284	2.04
Calculated MDL = Standard deviation x 3.14 = 0.558			
Calibration Check, QC-CN-WS, and Laboratory Method Blank (Sections 16.2, 16.4, 16.5)			
Calibration check	200	315,775	181
SPEX QC-CN-WS	204	308,906	177
Method blank	—	266	0.410
The provided QC-CN-WS acceptance range is 153 to 255 µg/L CN.			
Inject Each Sample Once and Report the Data Below for Samples 1 through 7			
Sample 1 (matrix blank)	—	1,772	1.22
Sample 2	Certified value = 400 µg/L	669,132	410
Sample 3	Certified value = 350 µg/L	582,357	351
Sample 4	Certified value = 130 µg/L	234,039	132
Sample 5	Certified value = 6 µg/L	12,506	7.03
Sample 6	Certified value = 5 µg/L	10,813	6.11
Sample 7	Certified value = 110 µg/L	203,438	115
Inject each sample in triplicate and report the data below for samples 8 and 9			
Sample 8 (replicate 1)	Fortified, biologically treated wastewater	117,993	65.4
Sample 8 (replicate 2)		117,531	65.1
Sample 8 (replicate 3)		118,115	65.5
Sample 9 (replicate 1)	Chlorinated, gold leaching, barren effluent	29,628	16.3
Sample 9 (replicate 2)		28,120	15.5
Sample 9 (replicate 3)		30,676	16.9
Calibration Check, QC-CN-WS, and Laboratory Method Blank (Sections 16.2, 16.4, 16.5)			
Calibration check	200	325,473	187
SPEX QC-CN-WS	204	313,188	180
Method blank	—	942	0.775

Hydrogen Cyanide Present or Generated During Fires

Because of the loss of life from inhalation of fire smoke gases, much attention has been given to analyses of these gases, which include HCN. This type of analysis must use a method that is free of interference to accurately estimate the amount of HCN that is present or generated during a fire. Fourier transform infrared spectroscopy (FTIR) is commonly used to measure HCN gases; however, the analysis of HCN by FTIR should not be regarded as an absolute measurement and may be subject to interference.

The concentration of hydrogen cyanide (HCN) generated during combustion of various solid materials can be accurately determined by sampling fire smoke gas into impingers containing 0.1 M NaOH. The impinger samples are then analyzed by FIA and amperometric detection using sulfide abatement reagent in the acidification reagent (1 M H_2SO_4). A draft ASTM standard is currently being reviewed by ASTM Committee D22 on Air Quality, and Committee E5 on Fire Standards is considering adding the procedure to Guide E800 for Measurement of Gases Present or Generated During Fires.

Approximately 175 fire smoke effluent samples were analyzed in accordance with the draft ASTM standard. The method was validated according to the Field Validation Protocol, USEPA Method 301. A reference material was burned in a cone calorimeter and sampled for HCN in duplicate along with duplicate spiked impingers. Table 6 shows an example of the results obtained with the FS 3100 and the ASTM draft standard.

Table 6. Statistical summary for HCN in smoke

Smoldering Conditions, Cone Calorimeter		
Sample	**Mean HCN (ppm)**	**% CN^- Recovery**
1	1.57	103
2	1.53	104
3	1.60	103
4	1.37	101
5	1.11	101
6	1.70	99.1
SD	*0.21*	*1.80*
Mean	*1.48*	*102*
% RSD	*14.3*	*1.77*
Bias	*0.03*	—
% Bias	*1.85*	—
Flame Conditions, Cone Calorimeter		
Sample	**Mean HCN (ppm)**	**% CN^- Recovery**
1	28.1	98.5
2	38.1	93.5
3	34.0	94.3
4	30.9	90.8
5	33.9	90.0
6	32.7	92.2
SD	*3.36*	*3.05*
Mean	*33.0*	*93.2*
% RSD	*10.2*	*3.27*
Bias	*–2.24*	—
% Bias	*–6.78*	—

Total Cyanide

Total cyanide can be determined with the FS 3100 instrument by distillation prior to analysis or by using online UV digestion as described in Method OIA-1678. Prior work has been done with distillation followed by FIA/amperometry with the laboratory's Flow Solution 3000 instrument. Distillations can be performed with either a midi-distillation apparatus (50-mL sample) or a Lachat Instruments MICRO DIST (6-mL sample). A draft standard was recently introduced to ASTM Committee D19 on Water in Reno, NV on June 15, 2005 and is expected to be reviewed on a subcommittee ballot this fall. This procedure improves upon classical USEPA methods that rely on pyridine-barbituric acid and colorimetry as the determinative step. By using a sulfide abatement reagent (bismuth nitrate) in the acidification reagent, sulfide interference is eliminated, and the need for additional lead acetate or lead carbonate scrubbers, which generally degrade method performance, is avoided. For example, a paper mill effluent sample's spike recovery can be vastly improved (>90%) compared to very low spike recovery with USEPA Method 335.2.

Approximately 20 samples were analyzed for total cyanide during the test period. Synthetic mining water samples from the aquatic free cyanide interlaboratory study were tested for total cyanide using MICRO DIST or midi-distillation followed by FIA with amperometric detection. All quality control data were acceptable; however, the synthetic test samples showed a positive bias (~50 µg/L CN^-), presumably, from the 15 mg/L SCN (thiocyanate). This interference, which would mainly affect the precious metals mining industry, was also observed with USEPA Method 335.2, confirming this problem is related to the distillation.

Method OIA-1678 could be used to analyze samples containing thiocyanate interference; however, this method was not evaluated on the FS 3100 during the beta test period.

Conclusion

The CNSolution FS 3100 system appears to be an improved version of the previous model. From the testing described in this poster, the new model appears to accurately determine available cyanide, total cyanide (after distillation), aquatic free cyanide, and hydrogen cyanide in fire smoke gases. The testing from this study indicates the instrument appears capable of satisfying the requirements of USEPA Method OIA-1677, ASTM D6888-04, and the new FIA/amperometry methods that are currently being standardized at the ASTM.

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