O·I·Analytical

CNSolution FS 3100 Initial Laboratory Test Results

Application Note 25211105

Keywords

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ASTM D6888-04
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Introduction

OI Analytical introduced the CNSolution FS 3100 flow injection analysis system (Figure 1) at Pittcon 2005. Following the conference, the FS 3100 system was installed for testing in an environmental analytical laboratory at Bayer MaterialScience LLC, Pittsburgh, PA. This application note presents the test report, which shows the exceptional quality of typical data that can be acquired on this improved FS 3100 flow injection analysis system for USEPA Method OIA-1677, ASTM D6888-04, and the new FIA/amperometry methods that are currently being standardized at the ASTM.

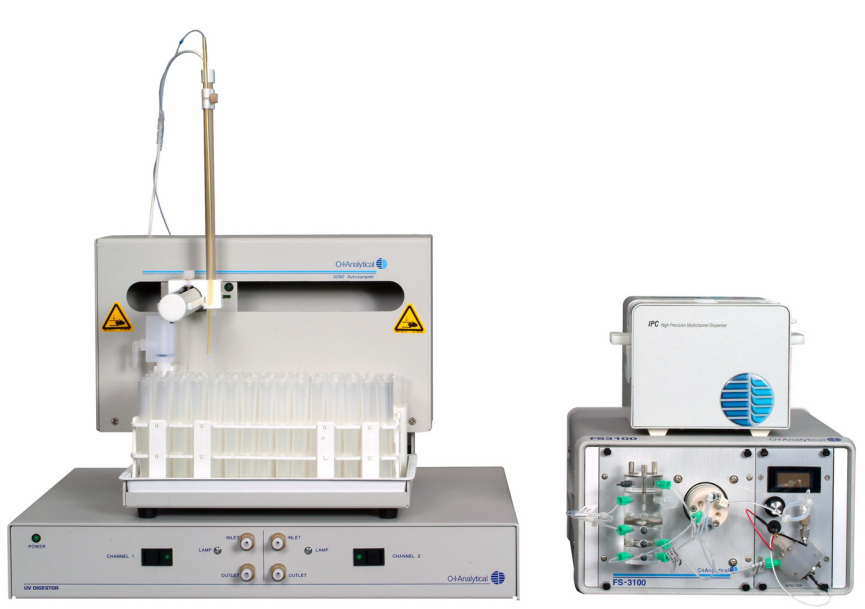

Figure 1. CNSolution FS 3100 flow injection analysis system with amperometric detector

Acknowledgement

OI Analytical thanks John R. Sebrowski and Bayer MaterialScience LLC of Pittsburgh, PA for their support and enthusiasm during this project. Customer feedback is an important and integral part of new instrument design, and we sincerely appreciate their participation in this process.

SYSTEM CERTIFICATION ISO 9001:2000 SGS

OI Analytical CNSolution™ FS3100 Beta Test Report

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Methods Evaluated

Available Cyanide

Approximately 200 samples (consisting of calibration standards, effluent samples, MS/MSD, quality control) were analyzed for available cyanide as described in US EPA 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 was determined by injecting a 2 μg/L standard seven times.

All quality control criteria from US EPA Method OIA-1677 and ASTM D6888-04 were met using the beta FS3100 instrument 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 below. Accuracy at 2 μg/L CN^- can be improved by narrowing the calibration standard range from 2 to 200 μg/L CN^-. It is also recommended to use a second order fit for the calibration curve. Typically, the reporting limit for available cyanide is 2 μg/L CN^-, which is the EPA minimum level (ML).

Available Cyanide Demonstration of Proficiency

Sample	Spike Concentration, ug/L	Concentration Found, ug/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 EPA OIA-1677.

Method Detection Limit

Sample	True Value, ug/L	Concentration Found, ug/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, ug/L	0.446
EPA Method ML, ug/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) is currently being developed by ASTM Committee D19 on Water. The method does not require ligand exchange reagents and utilizes a buffered acidification reagent at pH 6, pH 7, or pH 8. During the beta test, this method was validated with an interlaboratory study consisting of 9 labs. The round robin data will be evaluated for precision and bias according to ASTM D2777.

Since ASTM D2777 requires a reproducible sample matrix, synthetic precious metals mining 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 lab participants, who did not know the certified values at the time of the study. The intralaboratory data and our laboratory's results obtained with the FS3100 beta instrument are tabulated below.

Aquatic Free Cyanide Interlaboratory Statistical Summary

Sample	Mean, ug/L	RSD, %	True Value, ug/L	Mean Recovery, %
Calibration Check 200 ppb	196	5.81	200	98.1
Spex QC-CN-WS 204 ug/L	202	8.84	204	98.9
Method Blank	-0.241	-	0	-
Calculated MDL = Std. Dev. X 3.14	0.470	62.4	2	-
Calibration Check 200 ppb	196	8.89	200	98.0
Spex QC-CN-WS 204 ug/L	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 200 ppb	195	9.07	200	97.4
Spex QC-CN-WS 204 ug/L	198	12.7	204	97.0
Method Blank	-0.342	-	0	-

Data based on 8 reporting labs
Data from a 9th lab was not included due to instrument issues.

Aquatic Free Cyanide, ASTM Interlaboratory Study, Conducted with FS3100 Beta Unit

Sample	Instrument Response (pA)	Observed Result Aquatic Free CN, ug/L
Calibration Standards (Prepared in Section 8.8)		
Calibration Standard 0 ppb	-106	0.209
Calibration Standard 2 ppb	2478	1.60
Calibration Standard 5 ppb	9985	5.66
Calibration Standard 10 ppb	17481	9.72
Calibration Standard 20 ppb	37213	20.5
Calibration Standard 50 ppb	85234	47.0
Calibration Standard 100 ppb	185437	104
Calibration Standard 200 ppb	343162	198
Calibration Standard 500 ppb	797777	500
Calibration Check, QC-CN-WS, and Laboratory Method Blank (Sections 16.2, 16.4, 16.5)		
Calibration Check 200 ppb	325602	187
Spex QC-CN-WS 204 ug/L	349260	202
Method Blank	153	0.349
The provided QC-CN-WS accepance range is 153 to 255 ug/L CN		
Method Detection Limit Determination (Inject 2 ppb standard 7 times)		
2 ppb MDL 1	3651	2.24
2 ppb MDL 2	3783	2.31
2 ppb MDL 3	3543	2.18
2 ppb MDL 4	4366	2.62
2 ppb MDL 5	3609	2.21
2 ppb MDL 6	3717	2.27
2 ppb MDL 7	3284	2.04
Calculated MDL = Std. Dev. X 3.14	-	0.558
Calibration Check, QC-CN-WS, and Laboratory Method Blank (Sections 16.2, 16.4, 16.5)		
Calibration Check 200 ppb	315775	181
Spex QC-CN-WS 204 ug/L	308906	177
Method Blank	266	0.410
The provided QC-CN-WS accepance range is 153 to 255 ug/L CN		
Inject each sample once and report the data below for samples 1 through 7-		
Sample 1 (Matrix Blank)	1772	1.22
Sample 2 (Certified Value = 400 ppb)	669132	410
Sample 3 (Certified Value = 350 ppb)	582357	351
Sample 4 (Certified Value = 130 ppb)	234039	132
Sample 5 (Certified Value = 6 ppb)	12506	7.03
Sample 6 (Certified Value = 5 ppb)	10813	6.11
Sample 7 (Certified Value = 110 ppb)	203438	115
Inject each sample in triplicate and report the data below for samples 8 and 9-		
Sample 8 (Replicate 1)	117993	65.4
Sample 8 (Replicate 2)	117531	65.1
Sample 8 (Replicate 3)	118115	65.5
Sample 9 (Replicate 1)	29628	16.3
Sample 9 (Replicate 2)	28120	15.5
Sample 9 (Replicate 3)	30676	16.9
Calibration Check, QC-CN-WS, and Laboratory Method Blank (Sections 16.2, 16.4, 16.5)		
Calibration Check 200 ppb	325473	187
Spex QC-CN-WS 204 ug/L	313188	180
Method Blank	942	0.775

Total Cyanide

Total cyanide can be determined with the instrument by distillation prior to analysis or using an online UV digestion block as described in Method OIA-1678. Prior work has been done with distillation followed by flow injection / amperometry with the laboratory's FS3000 instrument. Distillations can be performed with either a midi-distillation apparatus (50-mL sample) or Lachat MicroDist™ (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 US EPA methods that rely on pyridine-barbituric acid and colorimetry as the determinative step. By utilizing 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%) in comparison to very low spike recovery with US EPA Method 335.2.

Approximately 20 samples were analyzed for total cyanide during the beta test period. Synthetic mining water samples from the aquatic free cyanide interlaboratory study were tested for total cyanide using MicroDist™ or midi-distillation followed by flow injection analysis 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 US EPA 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 be evaluated on the FS3100 since the UV digester was not included in the beta package. Further research needs to be conducted to determine if the UV digestion eliminates the positive bias observed from distillation.

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 the analyses of these gases including HCN. It is important to have a method that is free of interference in order to accurately estimate the amount of HCN that is present or generated during a fire. Fourier tranform 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) that is generated during the combustion of various solid materials can be accurately determined by sampling the fire smoke gas into impingers containing 0.1M NaOH. The impinger samples are then analyzed by flow injection analysis and amperometric detection using sulfide abatement reagent in the acidification reagent (1M 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 the Measurement of Gases Present or Generated During Fires.

During the beta test, 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, US EPA Method 301. A reference material was burned in a cone calorimeter and sampled for HCN in

duplicate along with duplicate spiked impingers. An example of the results obtained with the FS3100 beta unit and the ASTM draft standard is tabulated below.

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	-

General Conclusions

In general, the FS3100 CNSolution™ appears to be an improved version of the previous model. From the testing described in this report, 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 that the instrument appears to be capable of satisfying the requirements of US EPA Method OIA-1677, ASTM D6888-04, and the new FIA/Amperometry methods that are currently being standardized at ASTM.