

Simultaneous Analysis of Available and Total Cyanide by Gas Diffusion Amperometry Methods USEPA OIA-1677 and ASTM D 7511

William Lipps and Gary Engelhart • OI Analytical, P.O. Box 9010, College Station, TX 77842-9010 • (800) 653-1711

INTRODUCTION

USEPA methods OIA-1677¹ and ASTM D 7511² have the advantage of determining available cyanide and total cyanide respectively without a preliminary distillation step. These methods are usually run separately due to the manual ligand addition step required in OIA-1677 to release cyanide from certain metal-cyanide complexes. In this study, Method OIA-1677 was modified to automatically inject a diluted ligand reagent into the sample prior to determination. A modification to the TA1 reagent of ASTM D 7511 improves recovery of total cyanide, decreases interferences, and shares reagents with the available cyanide method. Automatic ligand injection enables total and available cyanide to be determined simultaneously from the same sample aliquot and using the same reagents.

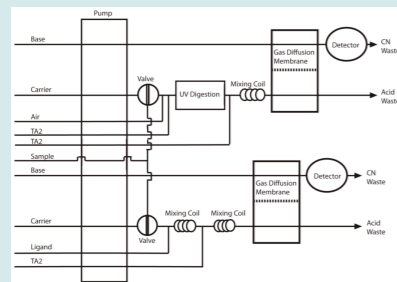
EXPERIMENTAL

A new cartridge based on the acidification reagents described in ASTM D 6888-09³ was designed to automatically add a diluted ligand exchange reagent solution to each sample injection. The ligand reagent is added in such small quantity that, even though flowing continuously, the approach saves money over manual addition.

The total cyanide cartridge for ASTM D 7511 was modified to use a single FEP UV digestion coil. This requires a lower flow rate for the TA1 acidification reagent. The TA1 reagent recipe was also modified from the original formulation achieving higher recoveries for total cyanide, and decreasing interferences from thiocyanate plus nitrate.

These modifications, allowed by 40 CFR Part 136.6 Method Flexibility; enable the analyst to share carrier, acidification, and acceptor reagents decreasing the overall complexity of the analysis. Sample solutions are merely poured into autosampler vials, and injected without any pretreatment. A tee splits the sample in half with one half directed to the total cyanide cartridge, and the other half directed to the available cyanide cartridge. See Figure 1 for a schematic flow diagram.

Figure 1. Flow Diagram of Dual Channel System for Simultaneous Analysis of Available and Total Cyanide



RESULTS & DISCUSSION

Total Cyanide

Prior to analysis of samples, each method modification was validated independently. The total cyanide method, ASTM D 7511 was reconfigured to a single FEP UV digestion coil in an effort to reduce cost and breakage of the quartz coils. The smaller inner diameter requires decreasing the flow-rate to ensure adequate exposure to the UV. The Teflon coil has a further advantage in its ability to be wound closer to the irradiation source increasing the efficiency of digestion. The acidification / digestion reagent, TA1, formulation was modified to further increase recovery from iron cyanide complexes, and decrease false positives that result when analyzing the ASTM D 7365 Challenge matrix. Table 1 is a summary of the validation results. All quantitation is by peak area.

Table 1. Validation of ASTM D 7511 Method Modifications

Analyte	ASTM D 7511 (µg/L CN)	ASTM D 7511 - Modified (µg/L CN)
100 ppb Iron (II) Complex	91.9	104
100 ppb Iron (III) Complex	89.4	104
100 ppb Prussian Blue	76.3	87.2
ASTM Challenge Matrix	44.2	21.6

In addition, six effluent samples containing very little available cyanide were analyzed and spiked with iron (III) cyanide at various concentrations. Table 2 summarizes the results of these tests.

Table 2. Analysis of Six Effluent Samples by ASTM D 7511 Using Modified TA1

	Sample Result Total Cyanide (µg/L)	Spiked Sample Result (µg/L)	% Recovery
Effluent 1	17.3	25.5	102
Effluent 2	262	438	88
Effluent 3	110	202	92
Effluent 4	12.2	27.3	109
Effluent 5	72.6	173	100
Effluent 6	81.5	177	95

Available Cyanide

OIA-1677 was configured to automatically add a diluted ligand reagent to the sample just prior to acidification. Because the ligand reagents can precipitate in acidic solution, the automatic addition can only be used if the alternative Sulfide Abatement Reagents are used. These are the same reagents as described in ASTM D 6888-09 and all, with the exception of the ligands, are also used for total cyanide by ASTM D 7511. This is advantageous as it allows each cartridge to share reagents reducing reagent preparation, decreasing the complexity of the simultaneous analysis, and decreasing the amount of bench space required.

RESULTS & DISCUSSION

Addition of the ligand as a dilute solution ensures that each sample is treated equally and decreases analyst manipulation of the sample. However, the maximum analytical range of the method is subsequently decreased to about 500 ppb available cyanide. Any samples containing weak metal-cyanide complexes at concentrations higher than 500 ppb should be diluted. Table 3 summarizes the validation of automated ligand injection. All quantitation is by peak area.

Table 3. Validation of Recovery of Nickel and Mercury Cyanide Complexes Using Automated Ligand Injection

Analyte	Available CN result (µg/L)	% Recovery
100 ppb [Ni(CN) ₄] ²⁻	95.5 (0.52%)	95.5
500 ppb [Ni(CN) ₄] ²⁻	446 (0.47%)	89.2
100 ppb HgCN ₂	101 (1.39%)	101
500 ppb HgCN ₂	491 (0.44%)	98.2

RSD in parentheses

While the slightly low recoveries for [Ni(CN)₄]²⁻ are within the specifications of the method, we suspect that the salt used for preparation of the nickel cyanide standard was impure causing the appearance of lowered recovery.

Simultaneous Analysis of Available and Total Cyanide

Once performance of each individual method was validated, a two-channel gas diffusion CNSolution 3100 system with amperometric detection was configured to run these two methods simultaneously.

Figure 2 shows the peak traces of a simultaneous analysis of total and available cyanide. Figure 3 and Figure 4 show each calibration respectively. Quality control samples containing a mixture of nickel cyanide [Ni(CN)₄]²⁻ and iron (III) cyanide [Fe(CN)₆]³⁻, and mercury cyanide HgCN₂ and iron (III) cyanide [Fe(CN)₆]³⁻ were analyzed. The nickel and mercury complex recovery demonstrate the effectiveness of Ligand reagents A&B, while the recovery of the Iron (III) cyanide complex demonstrates the efficiency of the total digestion/analysis. In addition, the ASTM D 7365 Challenge Matrix and three refinery effluents were analyzed. See Table 4 for a summary of the results.

Figure 2. Peak Traces of a Simultaneous Analysis of Total and Available Cyanide

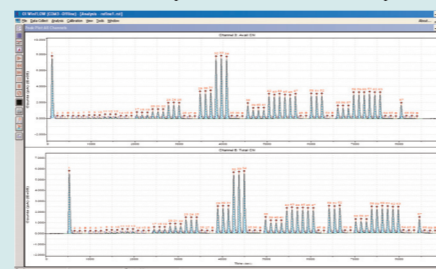


Figure 3. Eight-point Calibration for Total Cyanide Analysis by ASTM D 7511

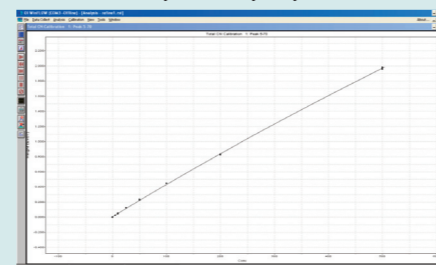
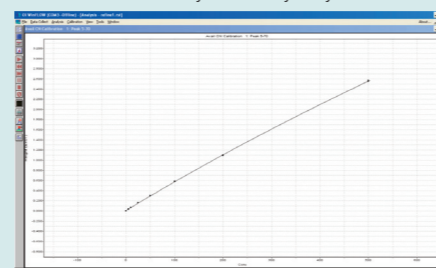


Figure 4. Eight-point Calibration for Available Cyanide Analysis by USEPA Method OIA-1677



RESULTS & DISCUSSION

Table 4. Summary of Simultaneous Total and Available Cyanide Results

Parameter	Available Cyanide by OIA-1677 (µg/L CN)	Total Cyanide by ASTM D 7511 (µg/L CN)
100 ppb Ni + 100 ppb Fe (III) CN complexes	97.7 (0.05%)	199 (0.42%)
100 ppb Hg + 100 ppb Fe (III) CN complexes	105 (0.07%)	218 (1.49%)
ASTM Challenge Matrix	< 0.5	19.9 (3.55%)
100 ppb CN	102 (0.38%)	99.8 (0.44%)
Refinery Sample #1	58.4 (0.70%)	76.5 (1.13%)
Refinery sample #2	158 (0.49%)	194 (1.17%)
Refinery Sample #3	73.7 (0.43%)	92.7 (3.27%)

RSD in parentheses

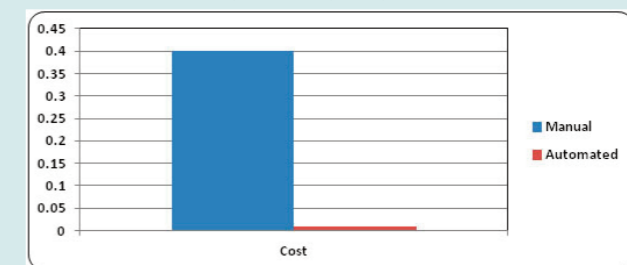
As expected, no available cyanide was detected in the ASTM Challenge Matrix, and the 19.9 ppb CN for total cyanide is typical for analysis using the D 7511 modified reagents. Recoveries of available cyanide and total cyanide confirm adequate method performance.

Cost Analysis

Both ASTM D 7511 and OIA-1677 methods, as configured, collect data for each injection every two minutes. This is a throughput of 30 samples per hour; however, since two tests are run simultaneously the actual throughput is 60 tests per hour. A laboratory running these methods could increase their capacity for an 8 hour shift from approximately 40 tests per day when using distillation methods to about 480 tests per day; a 10 fold increase in capacity. Because the methods do not require distillation, there are no costs, for disposable distillation labware, or associated manual labor.

Manual addition of ligands requires drop-wise addition of expensive ligand reagents to a known volume of sample. Often, to save time and money, ligands are not added. Manual ligand addition also restricts the analysis to a maximum of two hours after addition. Injecting a dilute solution of ligand only requires enough ligand for the very small amount of sample injected significantly reducing reagent costs. If scaled down to 10 milliliter volumes, the manual addition of ligands costs the laboratory \$0.40 per sample. Automated injection of a diluted solution of combined ligands costs the laboratory \$0.01 per sample; a 40 fold cost savings. See Figure 5 for an illustration of the cost savings by injecting the ligand.

Figure 5. Comparison of Costs for Manual and Automated Ligand Exchange Reagents Addition



Because the ligand is injected automatically, all samples, blanks, and standards are treated identically. Acidification and analysis takes place seconds after the ligand is added ensuring quantitative recovery of metal cyanide complexes and removing all time constraints in the method.

SUMMARY & CONCLUSIONS

The automated addition of ligand exchange reagent enables simultaneous analysis of available and total cyanide by methods OIA-1677 and ASTM D 7511. Using this approach laboratories can analyze available and total cyanide without preliminary sample treatments, such as manual ligand addition or distillation. A modification of the TA1 reagent formulation for ASTM D 7511 ensures quantitative recovery of iron cyanide complexes and minimizes interferences.

REFERENCES

1. Method OIA-1677 Available Cyanide by Flow Injection, Ligand Exchange, and Amperometry, EPA-821-R-99-013; U. S. Environmental Protection Agency, Office of Water, Engineering and Analysis Division, August 1999.
2. ASTM D 7511 "Standard Test Method for Total Cyanide by Segmented Flow Injection Analysis, In-Line Ultraviolet Digestion and Amperometric Detection", ASTM International, West Conshohocken, PA, www.astm.org.
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