Designation: D 6888 – 03

An American National Standard

# Standard Test Method for Available Cyanide with Ligand Displacement and Flow Injection Analysis (FIA) Utilizing Gas Diffusion Separation and Amperometric Detection[1]

This standard is issued under the fixed designation D 6888; the number immediately following the designation indicates the year of original adoption or, in the case of revision, the year of last revision. A number in parentheses indicates the year of last reapproval. A superscript epsilon (ε) indicates an editorial change since the last revision or reapproval.

## 1. Scope

1.1 This method is used to determine the concentration of available inorganic cyanide in an aqueous wastewater or effluent. The method detects the cyanides that are free (HCN and $CN^-$) and metal-cyanide complexes that are easily dissociated into free cyanide ions. The method does not detect the less toxic strong metal-cyanide complexes, cyanides that are not "amenable to chlorination."

1.2 This procedure is applicable over a range of approximately 2 to 400 µg/L (parts per billion) available cyanide. Higher concentrations can be analyzed by dilution or lower injection volume.

1.3 *This standard does not purport to address all of the safety concerns, if any, associated with its use. It is the responsibility of the user of this standard to establish appropriate safety and health practices and determine the applicability of regulatory limitations prior to use.* Specific hazard statements are given in Note 2 and Section 9.

## 2. Referenced Documents

2.1 *ASTM Standards:*

D 1129 Terminology Relating to Water[2]

D 1193 Specification for Reagent Water[2]

D 2036 Test Methods for Cyanides in Water[3]

D 2777 Practice for Determination of Precision and Bias of Applicable Methods of Committee D-19 on Water[2]

D 3370 Practices for Sampling Water[2]

D 3856 Guide for Good Laboratory Practices in Laboratories Engaged in Sampling and Analysis of Water[2]

D 4210 Practice for Intralaboratory Quality Control Procedures and a Discussion on Reporting Low-Level Data[2]

D 4375 Terminology for Basic Statistics in Committee D-19 on Water[2]

D 5847 Practice for Writing Quality Control Specifications for Standard Test Methods for Water Analysis[3]

D 6696 Guide for Understanding Cyanide Species[3]

E 60 Practice for Photometric and Spectrophotometric Methods for Chemical Analysis of Metals[4]

E 275 Practice for Describing and Measuring Performance of Ultraviolet, Visible, and Near Infrared Spectrophotometers[5]

E 1601 Practice for Conducting an Interlaboratory Study to Evaluate the Performance of an Analytical Method[5]

## 3. Terminology

3.1 *Definitions*—For definitions of terms used in this test method, refer to Terminology D 1129 and Guide D 6696.

3.2 *available cyanide*—Inorganic cyanides that are free (HCN and $CN^-$) and metal-cyanide complexes that are easily dissociated into free cyanide ions. Available cyanide does not include the less toxic strong metal-cyanide complexes, cyanides that are not "amenable to chlorination."

## 4. Summary of Test Method

4.1 Complex cyanides bound with nickel or mercury are released by ligand displacement by the addition of a ligand displacement agent prior to analysis.

4.2 Other weak and dissociable cyanide species do not require ligand displacement.

4.3 The treated sample is introduced into a flow injection analysis (FIA) system where it is acidified to form hydrogen cyanide (HCN). The hydrogen cyanide gas diffuses through a hydrophobic gas diffusion membrane, from the acidic donor stream into an alkaline acceptor stream.

4.4 The $CN^-$ is captured in the alkaline acceptor stream which then flows into an amperometric flowcell detector with a silver working electrode.

4.5 The cyanide oxidizes the silver electrode causing an amperometric current, which is detected. The current at any time is proportional to the concentration of cyanide flowing past the detector.

4.6 Calibrations and data are processed with the instrument's data acquisition software.

[1] This test method is under the jurisdiction of ASTM Committee D19 on Water and is the direct responsibility of Subcommittee D19.06 on Methods for Analysis of Organic Substances in Water.

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[2] *Annual Book of ASTM Standards*, Vol 11.01.

[3] *Annual Book of ASTM Standards*, Vol 11.02.

[4] *Annual Book of ASTM Standards*, Vol 03.05.

[5] *Annual Book of ASTM Standards*, Vol 03.06.

## 5. Significance and Use

5.1 Cyanide and hydrogen cyanide are highly toxic. Regulations have been established to require the monitoring of cyanide in industrial and domestic wastes and surface waters.[6]

5.2 This test method is applicable for natural water, saline waters, and wastewater effluent.

5.3 The method may be used for process control in wastewater treatment facilities.

5.4 The spot test outlined in Test Methods D 2036, Annex A1 can be used to detect cyanide and thiocyanate in water or wastewater, and to approximate its concentration.

## 6. Interferences

6.1 High levels of carbonate can release $CO_2$ into the acceptor stream and cause an interference with the amperometric detector that result in a slight masking effect (15 % negative bias with 20 ppb cyanide in 1500 ppm carbonate). Refer to 11.1 for sample pretreatment.

6.2 Sulfide will diffuse through the gas diffusion membrane and can be detected in the amperometric flowcell. Oxidized products of sulfide can also rapidly convert $CN^-$ to $SCN^-$ at a high pH. Refer to 11.3 for sulfide removal.

6.3 Refer to section 6.1 of Test Methods D 2036 for additional information regarding interferences for the analysis of cyanide and Section 11 of Test Methods D 2036 for elimination of interferences.

## 7. Apparatus

7.1 The instrument should be equipped with a precise sample introduction system, a gas diffusion manifold with hydrophobic membrane, and an amperometric detection system to include a silver working electrode, a Ag/AgCl reference electrode, and a Pt or stainless steel counter electrode. Examples of the apparatus schematics are shown in Figs. 1 and 2. Example instrument settings are shown in Table 1.[7]

NOTE 1—The instrument settings in Table 1 are only examples. The analyst may modify the settings as long as performance of the method has not been degraded. Contact the instrument manufacturer for recommended instrument parameters.

7.2 An autosampler is recommended but not required to automate sample injections and increase throughput. Autosamplers are usually available as an option from the instrument's manufacturer.

7.3 *Data Acquisition System*—Use the computer hardware and software recommended by the instrument manufacturer to control the apparatus and to collect data from the detector.

7.4 *Pump Tubing*—Use tubing recommended by instrument manufacturer. Replace pump tubing when worn, or when precision is no longer acceptable.

7.5 *Gas Diffusion Membranes*—A hydrophobic membrane which allows gaseous hydrogen cyanide to pervaporate from the donor to the acceptor stream at a sufficient rate to allow detection. The gas diffusion membrane should be replaced when the baseline becomes noisy or every 1 to 2 weeks.[8]

7.6 Use parts and accessories as directed by instrument manufacturer.

[6] 40 CFR Part 136.

[7] Both the ALPKEM CN Solution 3000 equipped with an amperometric flowcell, Available from O.I. Analytical, and Lachat Instruments QuikChem Automated Ion Analyzer using Method 10-204-00-5-A have been found to be suitable for this analysis.

[8] Gelmen Sciences Part Number M5PU025, ALPKEM Part Number A0015200, and Lachat Instruments Part Number 50398 have found to be suitable for this analysis.

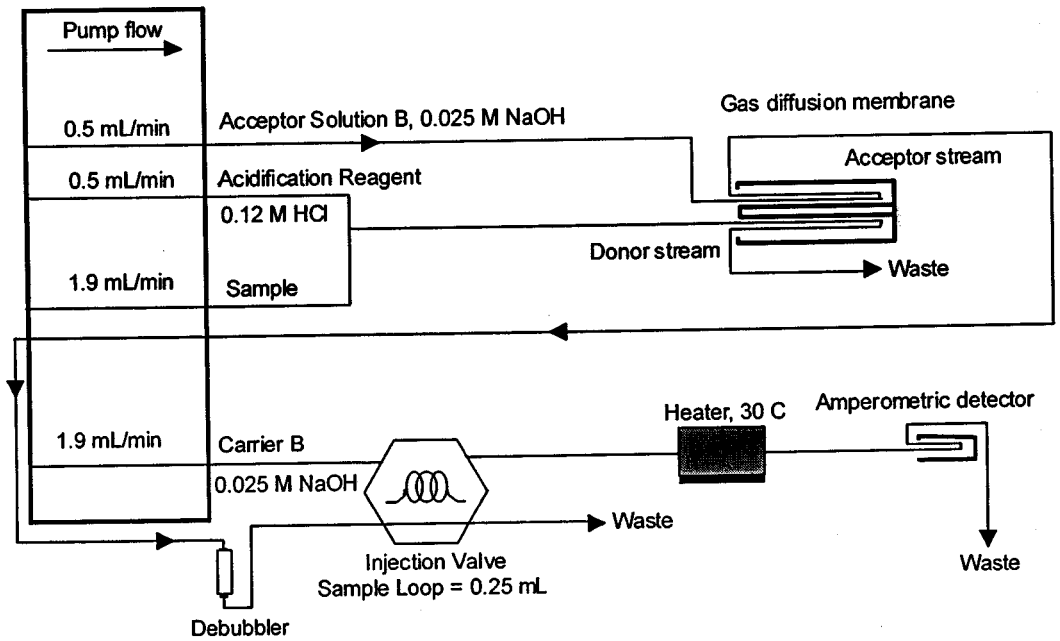


**FIG. 1 Flow Injection Analysis Apparatus 1**

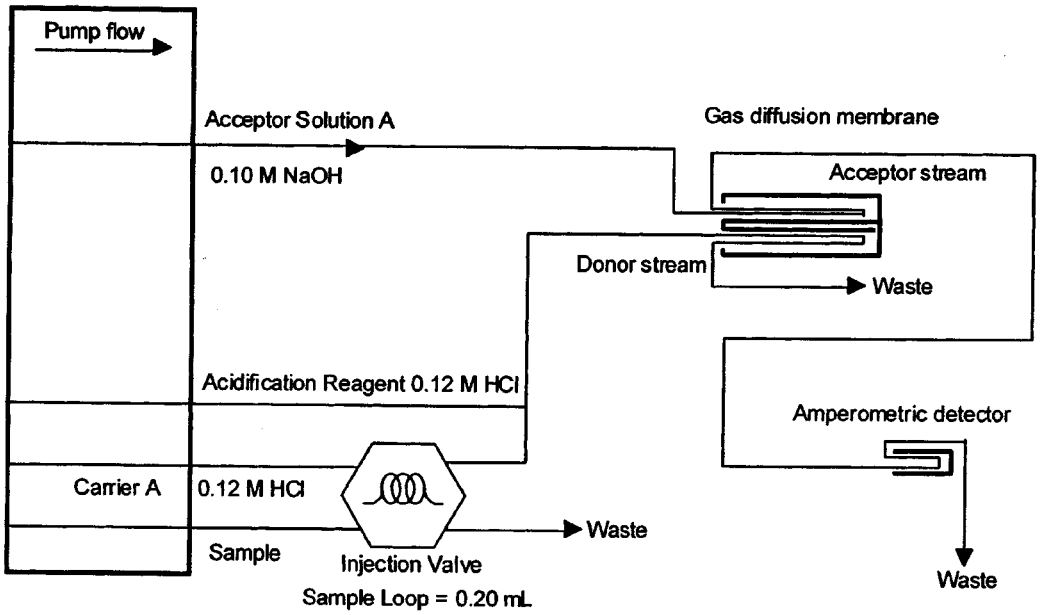


**FIG. 2 Flow Injection Analysis Apparatus 2**

**TABLE 1 Flow Injection Analysis Parameters**

| FIA Instrument Parameter | Recommended Method Setting |
|---|---|
| Pump Flow Rates | 0.5 to 2 mL/min |
| Cycle period (total) | 90 to 250 s/sample |
| Sample load period | At least enough time to completely fill the sample loop |
| Reagent water rinse time between samples | At least 15 s |
| Peak Evaluation | Peak height or area |
| Working Potential | 0.0 V vs Ag/AgCl |

## 8. Reagents and Materials

8.1 *Purity of Reagents*—Reagent grade chemicals shall be used in all tests. Unless otherwise indicated, it is intended that all reagents shall conform to the specifications of the American Chemical Society, where such specifications are available.[9] Other grades may be used, provided it is first ascertained that the reagent is of sufficiently high purity to permit its use without lessening the accuracy of the determination.

8.2 *Purity of Water*—Unless otherwise indicated, references to water shall be understood to mean reagent water conforming to Type II grade of Specification D 1193.

8.3 *Sodium Hydroxide Solution* (1.00 M)—Dissolve 40 g NaOH in laboratory water and dilute to 1 L.

8.4 *Acceptor Solution A* (0.10 M NaOH)—Dissolve 4.0 g NaOH in laboratory water and dilute to 1 L.

8.5 *Acceptor Solution B, Carrier B* (0.025 M NaOH)—Dissolve 1.0 g NaOH in laboratory water and dilute to 1 L.

8.6 *Stock Cyanide Solution* (1000 µg/mL $CN^-$)—Dissolve 2.51 g of KCN and 2.0 g of NaOH in 1 L of water. Standardize with silver nitrate solution as described in Test Methods D 2036, section 16.2. Store the solution under refrigeration and check concentration approximately every 6 months and correct if necessary.[10]

NOTE 2—**Warning:** Because KCN is highly toxic, avoid contact or inhalation.

8.7 *Intermediate Cyanide Standards*:

8.7.1 *Intermediate Standard 1* (100 µg/mL $CN^-$)—Pipette 10.0 mL of stock cyanide solution (see 8.6) into a 100 mL volumetric flask containing 1 mL of 1.0 M NaOH (see 8.3). Dilute to volume with laboratory water. Store under refrigeration. The standard should be stable for at least 2 weeks.

8.7.2 *Intermediate Cyanide Solution 2* (10 µg/mL $CN^-$)—Pipette 10.0 mL of Intermediate Cyanide Solution 1 (see 8.7.1) into a 100 mL volumetric flask containing 1.0 mL of 1.00 M NaOH (see 8.3). Dilute to volume with laboratory water. The standard should be stable for at least 2 weeks.

8.8 *Working Cyanide Calibration Standards*—Prepare fresh daily as described in 8.8.1 and 8.8.2 ranging in concentration from 2 to 400 µg/L $CN^-$.

8.8.1 *Calibration Standards* (20, 50, 100, 200, and 400 µg/L $CN^-$)—Pipette 20, 50, 100, 200, and 400 µL of Intermediate Standard 1 (see 8.7.1) into separate 100 mL volumetric flasks containing 1.0 mL of 1.00 M NaOH (see 8.3). Dilute to volume with laboratory water.

8.8.2 *Calibration Standards* (2 and 10 µg/L $CN^-$)—Pipette 20 and 100 µL of Intermediate Cyanide Solution 2 (see 8.7.2) into separate 100 mL volumetric flasks containing 1.0 mL of 1.00 M NaOH (see 8.3). Dilute to volume with laboratory water.

8.9 *Cyanide Shocking Solution* (Approximately 5 ppm as $CN^-$)—Pipette 500 µL of Stock Cyanide (see 8.6) into a 100

[9] *Reagent Chemicals, American Chemical Society Specifications*, Am. Chemical Soc., Washington, DC. For suggestions on the testing of reagents not listed by the American chemical Society, see *Analar Standards for Laboratory Chemicals*, BDH Ltd., Poole, Dorset, U.K., and the *United States Pharmacopeia*.

[10] Commerical Solutions of Stock Cyanide may be substituted.

mL volumetric flask containing 1.0 mL of 1.00 M NaOH (see 8.3). Dilute to volume with laboratory water. The solution should be stored under refrigeration.

8.10 *Acetate Buffer*—Dissolve 410 g of sodium acetate trihydrate ($NaC_2H_3O_2 \cdot 3H_2O$) in 500 mL of laboratory water. Add glacial acetic acid (approximately 500 mL) to yield a pH of 4.5.

8.11 *Carrier A and Acidification Reagent* (0.12 M HCl)—Transfer 10 mL of Trace Metal Grade concentrated hydrochloric acid into a 1 L volumetric flask. Carefully, dilute to volume with laboratory water.

8.12 *Ligand Exchange Reagent 1* (TEP Solution)—Weigh 0.10 g tetraethylenepentamine (TEP) into a 100 mL volumetric flask. Dilute to volume with laboratory water. The solution should be stored at room temperature.

8.13 *Ligand Exchange Reagent 2* (Dithizone Solution)—Weigh 0.010 g of dithizone into a 100 mL volumetric flask containing 1.0 mL of 1.00 M NaOH (see 8.3). Dilute to volume with laboratory water. Sonicate if necessary until all of the dithizone has dissolved. The solution should be stored at room temperature.

NOTE 3—Commercially prepared or alternative ligand exchange reagents can be used if equivalent results can be demonstrated. Commercial reagents should be used in accordance with manufacturer's instructions.[11]

8.14 *Mercury (II) Cyanide Stock Solution*—Weigh 0.4854 g $Hg(CN)_2$ into a 100 mL volumetric flask. Place 1.0 mL of 1.00 M NaOH (see 8.3) in the flask and dilute to volume with laboratory water. $Hg(CN)_2$ as $CN^-$= 1000 mg/L. The solution must be stored in an amber glass bottle under refrigeration at 4°C.

8.15 *Mercury (II) Cyanide Intermediate Solution*—Pipet 10.0 mL of the mercury (II) cyanide stock solution (see 8.14) into a 100 mL volumetric flask containing 1.0 mL of 1.00 M NaOH (see 8.3). Dilute to volume with laboratory grade water. $Hg(CN)_2$ as $CN^-$ = 100 mg/L. The solution must be stored in an amber glass bottle under refrigeration at 4°C.

8.16 *Mercury (II) Cyanide Recovery Solution*—Pipet 100 µL of mercury II cyanide intermediate solution (see 8.15) into a 100 mL volumetric flask containing 1.0 mL of 1.00 M NaOH (see 8.3). Dilute to volume with laboratory water. $Hg(CN)_2$ as $CN^-$ = 100 µg/L. Prepare fresh daily.

8.17 *Potassium Nickel Cyanide Stock Solution*—Weigh 0.2488 g of $K_2Ni(CN)_4$ $H_2O$ in a 100 mL volumetric flask. Place 1.0 mL of 1.00 M NaOH (see 8.3) in the flask and dilute to volume with laboratory water. $K_2Ni(CN)_4$ as $CN^-$ = 1000 mg/L. The solution must be stored in an amber glass bottle under refrigeration at 4°C.

8.18 *Potassium Nickel Cyanide Intermediate Solution*—Pipet 10.0 mL of the potassium nickel cyanide stock solution (see 8.17) into a 100 mL volumetric flask containing 1.0 mL of 1.00 M NaOH (see 8.3). Dilute to volume with laboratory grade water. $K_2Ni(CN)_4$ as $CN^-$ = 100 mg/L. The solution must be stored in an amber glass bottle under refrigeration at 4°C.

8.19 *Potassium Nickel Cyanide Recovery Solution*—Pipet 100 µL of potassium nickel cyanide intermediate solution (see 8.18) into a 100 mL volumetric flask containing 1.0 mL of 1.00 M NaOH (see 8.3). Dilute to volume with laboratory water. $K_2Ni(CN)_4$ as $CN^-$ = 100 µg/L. Prepare fresh daily.

8.20 *Ag/AgCl Reference Electrode Filling Solution*—Fill the reference electrode as recommended by the instrument manufacturer.

## 9. Hazards

9.1 **Caution—**Because of the toxicity of cyanide, great care must be exercised in its handling. Acidification of cyanide solutions produces toxic hydrocyanic acid (HCN). All manipulations must be done in the hood so that any HCN gas that might escape is safely vented.

9.2 **Warning—**Many of the reagents used in these test methods are highly toxic. These reagents and their solutions must be disposed of properly.

9.3 All reagents and standards should be prepared in volumes consistent with laboratory use to minimize the generation of waste.

## 10. Sample and Sample Preservation

10.1 Collect the sample in accordance with Practices D 3370 and D 3856.

10.2 The sample must be stablized at time of collection with the addition of sodium hydroxide (1 M is suitable for pH adjustment) until a pH of 12 to 12.5 is reached. See 11.1 if it is suspected that high levels of carbonate (>1500 ppm) are present in the sample.

10.3 Samples should be stored in dark bottles to minimize exposure to ultraviolet radiation, refrigerated at 4°C, and analyzed as soon as possible.

## 11. Elimination of Interferences

11.1 If samples are known to have high levels of $CO_3^{2-}$ (above 1500 ppm), preserve the sample by adding 2 g/L $Ca(OH)_2$ (hydrated lime) so that the pH is adjusted to pH > 12. Do not add NaOH to the sample as described in 10.2. Allow the $Ca(OH)_2/CaCO_3$ solids to settle to the bottom of the container prior to analysis.

11.2 *Oxidizing Agents*—Test for the presence of oxidizing agents. Add a drop of the sample to acidified KI starch test paper (acidify KI starch paper with acetate buffer, see 8.10) as soon as the sample is collected; a blue color indicates the need for treatment. If oxidizing agents are present, add 0.1 g/L sodium arsenite of sample to avoid degradation of cyanide.

11.3 *Sulfide*—Test for sulfide by placing a drop of sample on lead acetate paper previously moistened with acetate buffer solution (see 8.10). If the paper turns black, sulfide is present. Add lead acetate, or if the sulfide concentration is too high, add powdered lead carbonate to avoid significantly reducing the pH. Repeat this test until a drop of treated sample no longer darkens the acidified lead acetate test paper. The supernatant containing cyanide must be filtered immediately to avoid the rapid loss of cyanide due to the formation of thiocyanate.

## 12. Calibration and Standardization

12.1 Turn on the power to the apparatus and the autosampler (if equipped). Start the data acquisition system.

[11] ALPKEM WAD Reagents A and B, PN A0011416 and A0011417 have found to be suitable for this analysis.

12.2 Clamp the pump tube platens in place and start pumping reagents in the flow injection system. Allow the system to warm up at least 15 min or until a stable baseline is achieved. Take care not to over-tighten the pump tubes platens as this will greatly reduce their lifetime.

12.3 If recommended by the instrument manufacturer, aspirate the Cyanide Shocking Solution (5 ppm $CN^-$) from 8.9. After at least 30 s, inject the shocking solution into the apparatus and record the amperometric response (pA value) after the cycle period has completed. Repeat this procedure until the peak responses are less than 2 % RSD. This process will ensure that the electrode system has stabilized.

12.4 After the electrode system has stabilized, aspirate the highest working standard (see 8.8) into the flow injection apparatus. Follow the instrument manufacturer's instructions to store the retention time window for cyanide using the data acquisition software.

12.5 Pipette 100 µL of Ligand Exchange Reagent 1 (TEP) and 500 µL of Ligand Exchange Reagent 2 (Dithizone, see 8.13) into 10 mL of each working standard from 8.8 and swirl to a mix. Prepare a reagent blank for background correction if necessary.

NOTE 4—TEP addition alone will yield higher recoveries of mercury cyanide species than other methods; however, complete recovery is only possible with the addition of the dithizone reagent. If the samples are known to be free of mercury from historical data or if mercury analyses indicate the absence of mercury, the dithizone ligand exchange reagent may be omitted in the samples and working standards.

12.6 Inject each working standard and the reagent blank from 12.5 into the apparatus and record the amperometric response with the data acquisition system. Plot the response versus the cyanide concentration with a straight line or a quadratic fit curve depending on the instrument and data acquisition system employed. If the calibration model is polynomial, it may be no more than third order. A second order polynomial is recommended. An example of a calibration curve is shown in Fig. 3.

12.7 Prepare a new calibration curve at least once daily.

## 13. Procedure

13.1 Place 10 mL of each sample to be tested in separate polyethylene containers. Pipette 100 µL of Ligand Exchange Reagent 1 (TEP, see 8.12) and 500 µL of Ligand Exchange Reagent 2 (Dithizone, see 8.13) into the sample and swirl to mix.

13.2 Inject each sample into the flow injection apparatus, and inspect for irregular peak shapes, disturbances, or detector overloads. Dilute and re-run samples if necessary.

## 14. Data Analysis and Calculations

14.1 Report the cyanide as parts per billion (µg/L) available cyanide using the data acquisition software.

14.2 Multiply the result by any dilution factor and round the test result to three significant figures.

14.3 Some instruments are capable of performing multiple injections in which the mean result for each sample can be reported. In this case, the mean result should be reported.

## 15. Precision and Bias

15.1 Based on the results of 10 operators in 10 laboratories, the overall and single operator precision and method bias data are shown in Table 2. The precision and bias data were obtained from a synthetic wastewater and may not apply to all untested matrices.

15.2 This method was also evaluated and validated in a single laboratory. In the lab study, this procedure was found to be suitable for several natural and industrial matrices including coal strip mining water, surface water, spring water, river

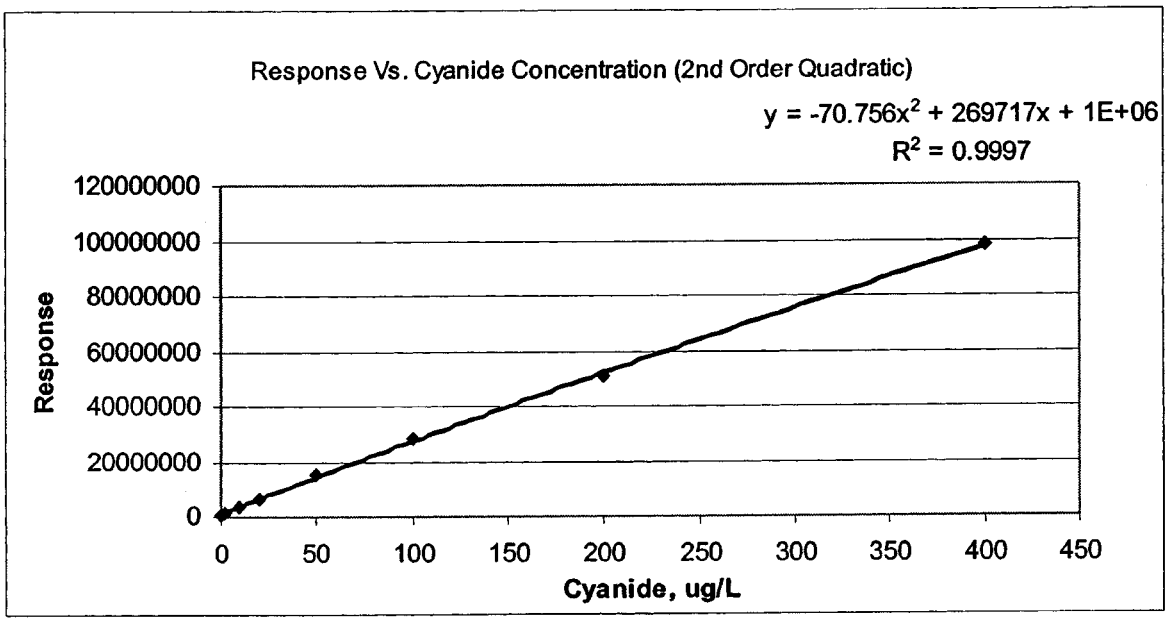


FIG. 3 Example of Calibration Curve

**TABLE 2 Precision and Bias for Available Cyanide**

| ASTM Test Method D 6888: Synthetic Wastewater—Final Statistical Summary for Available Cyanide Analyses | | | | | | |
|---|---|---|---|---|---|---|
| Sample Number | AC19721 | AC19723 | AC19726 | AC19722 | AC19724 | AC19725 |
| Number of retained values | 8 | 8 | 8 | 8 | 8 | 8 |
| True concentration (C), µg/L | 8.00 | 9.00 | 70.0 | 80.0 | 300 | 350 |
| Mean recovery (XBAR) | 7.10 | 8.32 | 64.2 | 71.5 | 266 | 315 |
| Percent recovery | 88.7 | 92.4 | 91.7 | 89.4 | 88.7 | 90.1 |
| Overall standard deviation ($S_T$) | 0.815 | 0.459 | 6.00 | 9.66 | 23.7 | 27.2 |
| Overall relative standard deviation, % | 11.5 | 5.52 | 9.35 | 13.5 | 8.92 | 8.63 |
| Number of retained pairs | 8 | | 8 | | 8 | |
| Single standard deviation ($S_o$) | 0.618 | | 4.39 | | 6.43 | |
| Analyst relative deviation, % | 8.02 | | 6.47 | | 2.21 | |

Synthetic Wastewater was prepared in 0.1 % synthetic sea salts.

water, treated municipal wastewater (POTW), industrial wastewater, groundwater, and drinking water. Recoveries of potassium nickel cyanide and mercury (II) cyanide (fortified with 100 µg/L as $CN^-$) ranged from 89.9 to 99.6 % and 82.9 to 99.3 %, respectively.[12]

## 16. Quality Assurance and Quality Control

16.1 In order to be certain that analytical values obtained using this test method are valid and accurate within the confidence limits of the test, the following QC procedures must be followed when running the test. For a general discussion of quality control and good laboratory practices, see Practice D 5847, Guide D 3856, and Practice D 4210.

16.2 *Calibration and Calibration Verification*:

16.2.1 Analyze the calibration standards daily prior to analysis to calibrate the instrument as described in Section 12.

16.2.2 Verify instrument calibration for each analytical batch of 10 samples by analyzing a mid-point standard. The recovery should be 90 to 110 % or else corrective actions should be taken.

16.3 *Initial Demonstration of Laboratory Capability*:

16.3.1 If a laboratory has not performed the test before or if there has been a major change in the measurement system, for example, new analyst, new instrument, etc., a precision and bias study must be performed to demonstrate laboratory capability.

16.3.2 Analyze seven replicates of a standard solution prepared from an independent reference material (IRM) containing 70 µg/L available cyanide. The matrix of the solution should be equivalent to the solution used in the collaborative study. Each replicate must be taken through the complete analytical procedure. The replicates may be interspersed with samples.

16.3.3 Calculate the mean and standard deviation of the seven values. The mean should range from 48.8 to 79.6 µg/L and the standard deviation should be less than 11.1, otherwise the study should be repeated until these criteria are met. If a concentration other than the recommended concentration is used, refer to Test Method D 5847 for information on applying the *F* test and *t* test in evaluating the acceptability of the mean and standard deviation.

16.4 *Laboratory Control Sample (LCS)*:

16.4.1 To ensure that the test method is in control, analyze a mercury(II) cyanide or potassium nickel cyanide recovery solution (see 8.16 and 8.19). The recoveries should be 81 to 121 % for mercury(II)cyanide and 90 to 117 % for potassium nickel cyanide or else corrective actions should be taken.

16.5 *Method Blank*:

16.5.1 Analyze a method blank with each batch of samples. A laboratory method blank can be prepared by adding 1.0 mL of 1.00 M NaOH (see 8.3) into a 100 mL volumetric flask and diluting to volume with laboratory water.

16.5.2 The measured concentration of available cyanide must be less than 2 µg/L. If the concentration is found above this level, analysis of samples is halted until the contamination is eliminated and a blank shows no contamination at or above this level, or the results should be qualified with an indication that they do not fall within the performance of the test method.

16.6 *Matrix Spike (MS)*:

16.6.1 To check for interferences in the specific matrix being tested, perform an MS on at least one sample from each batch by spiking an aliquot of the sample with a known concentration of cyanide and taking it through the analytical method. The spike must produce a concentration in the spiked sample 2 to 5 times the background concentration or 100 µg/L cyanide, whichever is greater. Cyanide matrix spikes can be prepared from the intermediate cyanide solutions- potassium cyanide (8.7.1), mercury cyanide (8.15), or potassium nickel cyanide (8.18). For example, partially fill a 100 mL volumetric flask with sample, add 100 µL of intermediate cyanide solution, then fill to volume with sample to produce a 100 µg/L cyanide matrix spike.

16.6.2 If the recovery is not within the limits as described in Practice D 5847, a matrix interference may be present in the sample selected for spiking. Under these circumstances, one of the following remedies must be employed: the matrix interference must be removed, all samples in the batch must be analyzed by a test method not affected by the matrix interference, or the results should be qualified with an indication that they do not fall within the performance criteria of the test method.

16.7 *Duplicate*:

16.7.1 To check the precision of sample analyses, analyze a sample in duplicate with each batch. If the concentration is less than five times the detection limit, an MS duplicate (MSD) should be used.

[12] Sebroski, Ode, "Method Comparison and Evaluation for the Analysis of Weak Acid-Dissociable Cyanide," *Environmental Science and Technology*, Vol 31, No. 1, 1997, pp. 52-57.

16.7.2 Calculate the standard deviation of the duplicate values and compare to the single operator precision from the collaborative study using an *F* test. Refer to 6.5.5 of Practice D 5847 for information on applying the *F* test.

16.7.3 If the result exceeds the precision limit, the batch must be reanalyzed or the results must be qualified with an indication that they do not fall within the performance criteria of the method.

16.8 *Independent Reference Material*:

16.8.1 In order to verify the quantitative value produced by the test method, analyze an IRM submitted as a regular sample (if practical) to the laboratory at least once per quarter. The concentration of the reference material should be in the range of this method. The value obtained must fall within the control limits specified by the outside source.

16.9 The analyst is permitted certain options to improve the performance of this method, provided that all performance specifications are met. These options include sample pretreatment to remove interferences and the use of alternative ligand exchange reagents. Any time such modifications are made, the Initial Demonstration of Proficiency must be successfully repeated.

## 17. Keywords

17.1 amperometry; available cyanide; cyanide; cyanide amenable to chlorination; flow injection analysis; free cyanide; gas diffusion membrane; ligand exchange; pervaporation; silver electrode; weak acid dissociable cyanide