METHOD 14561CN

Free Cyanide with Pyridine - Barbituric Acid and Photometry

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Acknowledgments

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Disclaimer

This method has been submitted to the U.S. Environmental Protection Agency for use in EPA's water programs but has not been approved for use by EPA. Mention of trade names or commercial products does not constitute endorsement or recommendation for use.

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Introduction

This method is a convenient, ready to use reagent test kit for cyanide (CN^-) testing, which is based on "Standard Methods for the Examination of Water and Wastewater," 18th edition, Method 4500 CN^- and "Chemical Analysis of Water and Wastewater" EPA Method 335.2. The test kit is suitable for both on-site testing and typical laboratory testing. The test kit consists of pre-measured reagent sets for analytical determinations. This method's approach with pre-measured reagents reduces analytical errors, the amount of hazardous waste, and increases occupational safety.

The method incorporates a range spanning 0.01 to 0.500 mg/L.

Method 14561CN

Free Cyanide with Pyridine - Barbituric Acid and Photometry

1.0 Scope and Application

1.1 Cyanide (CN) refers to all CN groups that can be determined as the Cyanide ion (CN^-). This cyanogen chloride-1,3-dimethyl barbituric acid method is based on the reaction of chlorinating agent dichloroisocyanuric acid with cyanide ions to form cyanogen chloride. This reacts with a pyridine compound, forming glutacone dialdehyde, which complexes 1,3-dimethyl barbituric acid to form a red-violet dye which is photometrically measured at or near 605 nm.

1.2 This method is for use in the United States Environmental Protection Agency's (EPA's) data gathering and monitoring programs under the Clean Water Act.

1.3 The method detection limit (MDL; 40 CFR 136, Appendix B) has been established at 0.003 mg/L (Section 13.2).

1.4 The Minimum Level (ML) for reporting results is 0.010 mg/L (Section 13.3).

1.5 This method is capable of measuring CN in the range of 0.01 to 0.500 mg/L.

1.6 This method measures CN^- (free cyanide) only. Samples must be pre-treated by distillation according the procedure outlined in Reference 16.1 or 16.2.

1.7 This method is intended for the analysis of CN on treated and untreated sanitary and industrial waste waters, and other waste water matrices.

1.8 This method is based on prior Environmental Protection Agency (EPA) and association methods for the determination of CN (references 16.1 and 16.2).

1.9 Each laboratory that uses this method must demonstrate the ability to generate acceptable results using the procedure in Section 9.2.

1.10 This method is capable of detecting CN in the range of 0.010 to 0.500 mg/L, and the range may be extended by serial dilution.

2.0 Summary of Method

2.1 Distill all samples according to current approved CN distillation techniques (References 16.1 and 16.2).

2.2 Prior to analysis, the pH of the pre-treated samples must be adjusted to between two and ten. This adjustment is critical to the color development.

2.3 After pH adjustment, five ml of the sample is transferred to a Spectroquant® Cell Test 14561, which contains dichloroisocyanuric acid reagent. The solid reagent is mixed with the sample by vigorous shaking until dissolved.

2.4 When the solid reagent in the cell is dissolved, add one dose (100 mg) of Spectroquant® Reagent CN-3K (pyridine carboxylic acid-1,3-dimethyl barbituric acid), close cell tightly, and shake to dissolve.

2.5 After allowing 10 minutes for the reaction period, measure the absorbance of the red-violet dye color complex using a Merck Spectroquant® system photometer (References 16.3, 16.4, and 16.5), or other photometric device at or near a wavelength of 605 nm.

2.6 Quality is assured through the use of quality control samples (QCS), calibration of the instrumentation by using calibration test solutions (CN std solution), and operation of a formal quality assurance program (Reference 16.6).

3.0 Definitions

Definitions for terms used in this method are given in the glossary at the end of the method (Section 18).

4.0 Interferences

4.1 All oxidizing and reducing agents can interfere, but are essentially eliminated with preliminary distillation.

4.2 Bromium interferes at a concentration of >0.1 mg/L (Reference 16.7).

4.3 Preliminary treatment (SM 4500 CN- B) does not decompose cobalt-cyano complexes; hence cobalt interferes at concentrations >1 mg/L (Reference 16.7).

4.4 Thiocyanate interferes if present at levels higher than 0.05 mg SCN^-/L, as it reacts similarly to (CN) (Reference 16.7).

4.5 Mercury (Hg^{2+}) interferes at concentrations >0.1 mg Hg^{2+}/L (Reference 16.7).

5.0 Safety

5.1 This method does not address all safety issues associated with its use. The toxicity or carcinogenicity of reagents used in this method has not been fully established. Each chemical and environmental sample should be regarded as a potential health hazard and exposure should be minimized. The laboratory is responsible for maintaining a safe work environment and a current awareness file of OSHA regulations regarding the safe handling of the chemicals specified in this method. A reference file of material safety data sheets (MSDSs) should be available to all personnel involved in these analyses. Additional information on laboratory safety can be found in References 16.3 and 16.4.

5.2 The toxicity or carcinogenicity of each reagent used in this method has not been precisely determined; however, each chemical should be treated as a potential health hazard. Exposure to these chemicals should be reduced to the lowest possible level. It is suggested that the laboratory perform personal hygiene monitoring of each analyst using this method and that the results of

this monitoring shall be made available to the analyst.

5.3 Samples of unknown origin may possess potentially hazardous compounds. Samples should be handled with care (e.g., under a hood), so as to minimize exposure.

5.4 As samples of unknown origin may contain compounds, which could react violently with the reagents, pipette the sample into the cell under a hood, and direct the opening of the cell away from anyone in the area.

5.5 This method employs the use of CN cell tests containing pre-measured reagents, which limits the handling of hazardous chemicals.

6.0 Equipment and Supplies

NOTE: *Brand names, suppliers, and part numbers are cited for illustrative purposes only. No endorsement is implied. Equivalent performance may be achieved using equipment and materials other than those specified here, but demonstration of equivalent performance that meets the requirements of this method is the responsibility of the laboratory.*

6.1 Sample collection bottles-1-L borosilicate amber glass or plastic.

6.2 Analytical balance-capable of weighing 0.1 mg.

6.3 Volumetric flasks-various sizes.

6.4 Volumetric pipettes-various sizes.

6.5 Reaction cells-Spectroquant® Cyanide Cell Test.

6.6 Laboratory timer.

6.7 Rack for cells.

6.8 Dry cloths for cleaning cell tests.

6.9 Photometric device.

6.9.1 Photometer capable of measuring absorbance at or near a wavelength of 605 nm, with cell compartment for tubes 16 x 100-mm-Merck Spectroquant® system photometer, or equivalent.

6.9.2 Spectrophotometer for use at 605-nm wavelength, with cell compartment for tubes 16 x 100 mm.

7.0 Reagents and Standards

7.1 Sodium Hydroxide (NaOH), ACS grade.

7.2 Spectroquant® CN Cell Test 14561, contains pre-measured dichloroisocyanuric acid reagent.

7.3 1,3 Dimethyl barbituric acid-pyridine carboxylic acid-Spectroquant® Reagent CN-3K.

7.4 Reagent water-deionized water.

7.5 CN stock solution (1,000 mg/L or 1ml = 1mg)-Spectroquant® catalog no. 1.19533, or equivalent.

7.6 CN intermediate solution (10 mg/L or 1 ml = 10 µg)-dilute 10 ml of CN stock solution to 1L in a volumetric flask.

7.7 CN std solution (1 mg/L or 1 ml = 1 µg)-dilute 10 ml of CN intermediate to 100 ml in volumetric flask. Prepare this solution fresh daily for calibration check.

7.8 Sample Preservation Reagents

7.8.1 The presence of sulfide may result in the conversion of cyanide to thiocyanate. While lead acetate test paper has been recommended for determining the presence of sulfide in samples, the test is generally unreliable and is typically not usable for sulfide concentrations below approximately 1 ppm. The use of lead carbonate, followed by immediate filtration of the sample is required whenever sulfide ion is present. If the presence of sulfide is suspected but not verifiable from the use of lead acetate test paper, two samples may be collected, one without lead carbonate addition and another with lead carbonate addition followed by immediate filtration. Analyze both samples. If sulfide is present, the preserved sample should contain higher levels of cyanide than the un-preserved sample. Lead acetate test paper may be used, but should be tested for minimum level of sulfide detection by spiking reagent water aliquots with decreasing levels of sulfide and determining the lowest level of sulfide detection obtainable. The spiked samples are tested with lead acetate test paper moistened with acetate buffer solution. The buffer solution is prepared by dissolving 146 g anhydrous sodium acetate, or 243 g sodium acetate trihydrate in 400 mL of reagent water (Section 7.4), followed by addition of 480 g concentrated acetic acid. Dilute the solution to 1 L with reagent water. Each new batch of test paper and/or acetate buffer should be tested to determine the lowest level of sulfide ion detection prior to use.

7.8.2 Ethylenediamine solution—In a 100 mL volumetric flask, dilute 3.5 mL pharmaceutical-grade anhydrous ethylenediamine with reagent water (Section 7.4).

7.8.3 Ascorbic acid—Crystals

8.0Sample Collection, Preservation, and Storage

8.1 Sample collection and preservation—Samples are collected using manual (grab) techniques (Reference 16.10) and are preserved immediately upon collection.

8.1.1 Grab sampling—Collect samples in amber glass bottles with PTFE-lined caps. Immediately after collection, preserve the sample using any or all of the special preservation techniques (Section 8.2) followed by adjustment of the sample pH to 12 by addition of 1M sodium hydroxide and refrigeration at 0-4°C.

8.1.2 Compositing—Compositing is performed by combining aliquots of grab samples only. Automated compositing equipment may not be used because cyanide may react or degrade during the sampling period. Preserve and refrigerate each grab sample immediately after collection (Sections 8.1.1 and 8.2) until compositing.

8.1.3 Shipment—If the sample will be shipped by common carrier or mail, limit the pH to a range of 12.0 - 12.3. (See the footnote to 40 *CFR* 136.3(e), Table II, for the column

headed "Preservation.")

8.2 Special preservation techniques.

8.2.1 Samples containing sulfide ion—Test samples with lead acetate test paper (Section 7.7.1) to determine the presence or absence of sulfide ion. If sulfide ion is present, treat the sample with sufficient solid lead carbonate (Section 7.7.1) to remove sulfide (as evidenced by lead acetate test paper) and immediately filter into another sample bottle to remove precipitated lead sulfide. If sulfide ion is suspected to be present, but its presence is not detected by this test, two samples should be collected. One is treated for the presence of sulfide and immediately filtered, while the second sample is not treated for sulfide. Both samples must be analyzed by the laboratory. Tests have been conducted which showed significant and rapid losses of cyanides when lead sulfide was allowed to remain in contact with the sample during holding times of three days and less. As a result, the immediate filtration of samples preserved with lead carbonate is essential.

8.2.2 Samples containing water soluble aldehydes—Treat samples containing or suspected to contain formaldehyde, acetaldehyde, or other water soluble aldehydes with 20 mL of 3.5% ethylenediamine solution (Section 7.7.2) per liter of sample.

8.2.3 Samples known or suspected to contain chlorine, hypochlorite, and/or sulfite—Treat with 0.6 g of ascorbic acid (Section 7.7.3) per liter of sample.

8.3 Sample holding time—Maximum holding time for samples preserved as above is 14 days. Unpreserved samples must be analyzed within 24 hours, or sooner if a change in cyanide concentration will occur. (See the footnotes to Table II at 40 *CFR* 136.3(e).)

8.4 Collect an additional two aliquots of a sample for each batch (of at least 20 samples) for the matrix spike and matrix spike duplicate.

9.0 Quality Control

9.1 Each laboratory using this method is required to operate a formal quality control (QC) program. The minimum requirements of this program consist of an initial demonstration of laboratory capability, and the ongoing analysis of laboratory reagent blanks, precision and recovery standards, and matrix-spiked samples as a continuing check on performance. The laboratory is required to maintain performance records that define the quality of data thus generated. Laboratory performance is compared to established performance criteria to determine if the results of analyses meet the performance characteristics of the method.

9.1.1 The analyst shall make an initial demonstration of the ability to generate acceptable accuracy and precision with this method. This ability is established as described in Section 9.2.

9.1.2 Analysis of matrix spike and matrix spike duplicate samples are required to demonstrate method accuracy and precision and to monitor matrix interferences (interferences caused by the sample matrix). The procedure and QC criteria for spiking are described in Section 9.3.

9.1.3 Analyses of laboratory blanks is required to demonstrate freedom from contamination. The procedure and criteria for blank analyses is described in Section 9.4.

9.1.4 The laboratory shall, on an ongoing basis, demonstrate through calibration verification and analysis of the ongoing precision and recovery sample that the analysis system is in control. These procedures are described in Sections 9.5 and 9.6.

9.1.5 The laboratory shall maintain records to define the quality of data that is generated. Development of accuracy statements is described in Sections 9.3.7 and 9.6.3.

9.1.6 Accompanying QC for the determination of CN is required per analytical batch. An analytical batch is a set of samples analyzed, to a maximum of 20 samples. Each analytical batch, of up to 20 samples, must be accompanied by a laboratory blank (Section 9.4), and ongoing precision and recovery sample (OPR, Section 9.6), and a matrix spike and matrix spike duplicate (MS/MSD, Section 9.3).

9.2 Initial demonstration of laboratory capability-The initial demonstration of laboratory capability is used to characterize laboratory performance and method detection limits.

9.2.1 Method detection limit (MDL)-The method detection limit must be established for the analyte, using the CN standard solution (Section 7.7). To determine MDL values, take seven replicate aliquots of the diluted CN standard solution and process each aliquot through each step of the analytical method. Perform all calculations and report the concentration values in the appropriate units. MDLs should be determined every year or whenever a modification to the method or analytical system is made that will affect the method detection limit.

9.2.2 Initial Precision and Recovery (IPR) - To establish the ability to generate acceptable precision and accuracy, the analyst shall perform the following operations:

9.2.2.1 Analyze four samples of the CN std solution (Section 7.7) according to the procedure beginning in Section 11.

9.2.2.2 Using the results of the four analyses, compute the average percent recovery (x) and the standard deviation (s, Equation 1) of the percent recovery for CN.

Equation 1

$$s = \sqrt{\frac{\sum x^2 - \frac{(\sum x)^2}{n}}{n-1}}$$

Where:

n = number of samples

x = % recovery in each sample

s = standard deviation

9.2.2.3 Compare s and x with the corresponding limits for initial precision and recovery in Section 17, Table 3 (Reference 16.11), which lists EPA's proposed standardized QC and QC Acceptance Criteria for Methods in 40 CFR Part 136, Table IB. If s and x meet the acceptance criteria, system performance is acceptable and analysis of samples may begin. If, however, s exceeds the precision limit or x falls outside the range for recovery, system performance is unacceptable. In this event, correct the problem, and repeat the test.

9.3 Matrix Spikes-The laboratory must spike, in duplicate, a minimum of five percent of all samples (one sample in each batch of 20 samples). The two sample aliquots shall be spiked with the CN std solutions (Section 7.7).

9.3.1 The concentration of the spike in the sample shall be determined as follows:

9.3.1.1 If, as in compliance monitoring, the concentration of CN in the sample is being checked against a regulatory concentration limit, the spiking level shall be at that limit or at 1 to 5 times higher than the background concentration of the sample (determined in Section 9.3.2), whichever concentration is higher.

9.3.1.2 If the concentration of CN in a sample is not being checked against a limit, the spike shall be at the concentration of the precision and recovery standard (Section 7.7), or at 1 to 5 times higher than the background concentration, whichever concentration is higher.

9.3.2 Analyze one sample aliquot out of each set of 20 samples, according to the procedure beginning in Section 11, to determine the background concentration (B) of CN.

9.3.2.1 If necessary, prepare a standard solution appropriate to produce a level in the sample at the regulatory compliance limit or at 1 to 5 times the background concentration (per Section 9.3.1).

9.3.2.2 Spike two additional sample aliquots with the CN standarsd solution and analyze these aliquots to determine the concentration after spiking (A).

9.3.3 Calculate the percent recovery (P) of CN in each aliquot using the following equation:

Equation 2

$$P = 100 * \frac{(A - B)}{T}$$

where:

P=Percent recovery

A=Measured concentration of CN after spiking

B=Measured concentration of CN before spiking

T=True concentration of the spike

9.3.4 Compare the percent recovery of the CN with the corresponding QC acceptance criteria in Section 17, Table 3 (Reference 16.11), which lists EPA's standardized QC and QC Acceptance Criteria for Methods in 40 CFR Part 136, Table IB.

9.3.4.1 If the results of the spike fail the acceptance criteria, and the recovery of the QC standard in the ongoing precision and recovery test (Section 9.6) for the analytical batch is within the acceptance criteria in Section 17, Table 3 (Reference 16.11), an interference is present. In this case, the result may not be reported for regulatory compliance purposes and the analyst must assess the potential cause for the interference. If the interference is attributable to sampling, the site or discharge should be resampled. If the interference is attributable to a method deficiency, the analyst must modify the method repeat the tests required in Section 9.1.2, and repeat the analysis of the sample and the MS/MSD.

9.3.4.2 If the results of both the spike and the ongoing precision and recovery test fail the acceptance criteria, the analytical system is judged to be out of control, and the problem shall be identified and corrected, and the sample re-analyzed.

9.3.5 Compute relative percent difference (RPD) between the two results (not between the two recoveries) using the following equation:

Equation 3

$$RPD = 100 * \frac{(|D_1 - D_2|)}{(D_1 + D_2)/2}$$

where:

RPD=Relative percent different

D_1=Concentration of CN in the sample

D_2=Concentration of CN in the second (duplicate) sample

9.3.6 The relative percent difference for duplicates shall meet the acceptance criteria in Section 17, Table 3 (Reference 16.11). If the criteria are not met, the analytical system is judged to be out of control, and the problem must be immediately identified and corrected, and the analytical batch re-analyzed.

9.3.7 As a part of the QC program for the laboratory, method precision and accuracy for samples should be assessed and records should be maintained. After the analysis of five spiked samples, in which the recovery passes the test in Section 9.3.4, compute the average percent recovery (P_a) and the standard deviation of the percent recovery (s_p). Express the accuracy assessment as a percent recovery interval from P_a-2s_p to P_a+2s_p. For example, if P_a = 90% and s_p = 10% for five analyses of CN, the accuracy interval is expressed as 70-110%. Update the accuracy assessment on a regular basis (e.g., after each five to ten new accuracy measurements).

9.4 Laboratory blanks-Laboratory reagent water blanks are analyzed to demonstrate freedom from contamination.

9.4.1 Prepare and analyze a laboratory blank initially (i.e., with the tests in Section 9.2) and with each analytical batch. The blank must be subjected to the same procedural steps as a sample.

9.4.2 If material is detected in the blank at a concentration greater than the ML (Section 1.3), analysis of samples must be halted until the source of contamination is eliminated and a new blank shows no evidence of contamination. All samples must be associated with an uncontaminated laboratory blank before the results may be reported for regulatory compliance purposes.

9.5 Calibration verification-Verify calibration of the photometric device per Section 10 for each analytical batch of up to 20 samples. If calibration curve linearity differs more than 10%, run a new calibration curve.

9.6 Ongoing Precision and Recovery (OPR)-To demonstrate that the analysis system is in control, and acceptable precision and accuracy is being maintained with each analytical batch, the analyst shall perform the following operations:

9.6.1 Analyze a precision and recovery standard (Section 7.7) with each analytical batch according to the procedure beginning in Section 11.

9.6.2 Compare the concentration with the limits for ongoing precision and recovery in Section 17, Table 3 (Reference 16.11). If the concentration is in the range specified, the analysis may proceed. If however, the concentration is not in the specified range, the analytical process is not in control. In this event, correct the problem, repeat the analytical batch, and repeat the ongoing precision and recovery test.

9.6.3 The laboratory should add results that pass the specification in Section 9.6.2 to IPR and previous OPR data and update QC charts to form a graphic representation of continued laboratory performance. The laboratory should also develop a statement of laboratory data quality for each analyte by calculating the average percent recovery (R) and the standard deviation of the percent recovery (s_r). Express the accuracy as a recovery interval from R - $2s_r$ to R + $2s_r$.

For example, if R = 95%, and s_r = 5%, the accuracy is 85 % to 105 %.

9.7 Quality control sample (QCS)–It is suggested that the laboratory obtain a quality control sample from a source different from the source of the CN used routinely in this method (Section 7.7).

9.8 The standards used for initial precision and recovery (IPR, Section 9.2.2) matrix spikes (MS/MSD, Section 9.3), and ongoing precision and recovery (OPR, Section 9.6) should be identical, so that the most precise results will be obtained.

10.0 Calibration and Standardization

10.1 Merck Spectroquant® system photometers are shipped factory calibrated (Reference 16.12), refer to the manufacturer's documents (References 16.3, 16.4, and 16.5). The calibration curve can be verified, and the data from this verification can be stored, modified or re-entered at anytime. However, the factory program settings cannot be changed by the user. When appropriate, the manufacturer supplies a new MemoChip (transponder) containing new calibration data.

10.2 For absorbance measurements using the Merck Spectroquant® photometric equipment, or other photometric devices, plot a calibration curve with a minimum of five (5) data points, from standards prepared from a CN solution appropriate to the range to be tested. The calibration curve should also include a blank.

10.2.1 For Spectroquant® CN cell test item 14561, prepare a standard curve from the CN std solution (Section 17.0, Table 2). The curve should include the lowest and highest concentrations for the range tested.

10.3 Verify the curve, using a calibration standard (mid-point of the curve), with each analytical batch of samples (Section 9.5).

10.4 Run a new calibration curve with each new lot of reagents, or when calibration curve linearity differs more than 10%, as stated in 40 CFR part 136, Table IB (Section 9.5).

11.0Procedure

11.1 Distill all samples using the procedures outlined in SM 4500 CN.

11.2 Adjust the pH of distillate to pH between two and ten prior to measurement.

11.3 Measure five ml of pH adjusted, pre-treated sample into a Spectroquant® CN Cell Test 14561. Cap tightly, and shake vigorously until the solid material is dissolved.

11.4 Add one dose (100 mg) of Spectroquant® Reagent CN-3K. Cap tightly, and shake the cell vigorously to dissolve the reagent.

11.5 Wipe the cell clean with a clean dry cloth, and place cell in rack, and wait ten minutes for the color reaction to complete.

11.6 Determination using Merck Spectroquant® system photometer.

11.6.1 Switch on the Merck Spectroquant® system photometer as per manufacturer's suggestions for operation (References 16.3, 16.4, and 16.5).

11.6.2 Place the Spectroquant® CN cell test into the cell compartment with the vertical line aligned with the notch on the instrument. Push down until the cell clicks into place.

11.6.3 Wait as the Merck Spectroquant® system photometer recognizes the bar code. The Spectroquant® CN Cell Test product information is displayed, and the instrument is automatically set to the appropriate wavelength and measuring parameters (bar code recognition of item number, test range, cell format, wavelength, and calibration data).

11.6.4 Record the displayed result in mg CN/L.

11.7 Determination using absorbance mode of the Merck Spectroquant® system photometer, or equivalent photometric device.

11.7.1 Warm up the instrument as per manufacturer's suggestion for operation.

11.7.2 Set the instrument to wavelength at or near 605 nm for the Spectroquant® CN cell test 14561.

11.7.3 Zero the instrument with a reagent water / blank which has been prepared in the same manner as the standards and samples.

11.7.4 Place the cell into the cell compartment/cell holder with the vertical line facing you.

11.7.5 Record the absorbance reading on the instrument.

11.7.6 Plot the absorbance reading on the calibration curve, to obtain the concentration CN as mg/L.

12.0 Data Analysis and Calculations

12.1 If pre-dilution and distillation were not performed upon the sample, no calculation is necessary.

12.2 If pre-dilution was required, calculate the CN (mg/L) as follows:

Equation 4

$$CN = A * \frac{V_2}{V_1}$$

where:

A = Measured concentration of CN from photometer (mg/L)

V_1 = Volume of sample used for dilution (ml)

V_2 = Final total volume of diluted sample (ml)

12.3 For samples which have been distilled, calculate the concentration of CN in the sample as in Equation 5.

Equation 5

$$CN, mg/L = A\left(\frac{B}{C}\right)$$

where:

A = Measured concentration of CN from photometer (mg/L)

B = Initial volume of sample distilled (ml)

V_2 = final distillation volume (ml)

12.4 Report results to three significant digits for concentrations found above the ML (Section 1.4) in all samples. Report results below the ML as <0.010 mg/L for CN.

13.0Method Performance

13.1 This method, as equivalent to Standard Method 4500 CN-E (Reference 16.1) should achieve the method performance as cited in Section 6 of that method.

13.2 The method detection limit (MDL) study was performed by a single analyst, and was determined as 0.003 mg/L.

13.3 The minimum level (ML) is determined as 0.01 mg/L.

14.0 Pollution Prevention

14.1 The reagents used in this method pose little threat to the environment, when managed properly.

14.2 Reagents should be ordered consistent with laboratory use, to minimize the amount of expired materials to be disposed.

15.0 Waste Management

15.1 It is the laboratory's responsibility to comply with all federal, state, and local regulations governing waste management, particularly the hazardous waste identification rules and land disposal restriction. The Agency urges laboratories to protect the air, water, and land by minimizing and controlling all releases from hoods and bench operations, complying with the letter and spirit of any sewer discharge permits and regulations.

15.2 For further information on waste management, consult "The Waste Management Manual for Laboratory Personnel" and "Less is Better: Laboratory Chemical Management for Waste Reduction," both available from the American Chemical Society's Department of Government Relations and Science Policy, 1155 16th Street N.W., Washington, D.C. 20036.

16.0 References

16.1 "Standard Methods for the Examination of Water and Wastewater," 18th Edition, American Public Health Association, 1015 Fifteenth Street, N.W., Washington, D.C. 20005, Method 4500-CN E.

16.2 "Methods for the Chemical Analysis of Water and Wastes," 3rd Edition, Environmental Protection Agency, Environmental Monitoring Systems Laboratory–Cincinnati (EMSL–Ci), Cincinnati, Ohio 45268, EPA–600/4-79-020, Method 335.2.

16.3 Spectroquant® SQ 118 Manual, Merck KGaA, Frankfurter Strasse 250, Darmstadt 64271, Germany, Release July 1998.

16.4 Spectroquant® NOVA 60 Manual, Merck KGaA, Frankfurter Strasse 250, Darmstadt 64271, Germany, Release July 1998.

16.5 Spectroquant® VEGA 400 Manual, Merck KGaA, Frankfurter Strasse 250, Darmstadt 64271, Germany, Release July 1998.

16.6 "Handbook of Analytical Quality Control in Water and Wastewater Laboratories," USEPA, EMSL-Ci, Cincinnati, OH 45268, EPA-600/4-79-019, March 1979.

16.7 Spectroquant® CN Cell Test Product Insert Sheet, Item 14561, Merck KGaA, Frankfurter Strasse 250, Darmstadt 64271, Germany, Release June 1999.

16.8 "OSHA Safety and Health Standards, General Industry," (29CFR 1910), Occupational Safety and Health Administration, OSHA 2206, revised January 1976.

16.9 "Safety in Academic Chemistry Laboratories," American Chemical Society Publication, Committee on Chemical Safety, 3rd Edition, 1979.

16.10 "Standard Methods for the Examination of Water and Wastewater," 18th Edition, American Public Health Association, 1015 Fifteenth Street, N.W., Washington, D.C. 20005, Method 1060.

16.11 Protocol for EPA Approval of Alternate Test Procedures for Organic and Inorganic Analytes in Wastewater and Drinking Water-Draft March 1998, Environmental Protection Agency, Office of Water (4303) Washington, DC 20460.

16.12 "German Standard Methods for the Examination of Water, Wastewater, and Sludge," Deutsches Institut fhr Normung e.V., D-10772, Berlin, DIN Method 38402 Part 51, May 1986.

17.0 Tables and Validation Data

Table 1. Product Range, Number, and Usage Information

Range mg/L	Cell Type (mm)	Sample Volume (ml)
0.010 - 0.500	16 x 100	5

Table 2. Calibration Standard Calibration Preparation

Product # Range (mg/L)	CN Std Solution Volumes (ml)*	CN Equivalent (mg/L)
0.010 - 0.500	0-1.0-10-25-40-50	0-0.010-0.100-0.250-0.400-0.500

* Dilute all working calibration standards to 100 ml in volumetric flasks.

Table 3. Acceptance Criteria for Performance Tests

Acceptance Criterion	Section	Limit (%)
Initial precision and recovery	9.2.2	
CN Precision (s)	9.2.2.2	30
CN Recovery (X)	9.2.2.2	47 - 153
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18.0Definitions

18.1 The definitions and purposes are specific to this method, but have been conformed to common usage as much as possible.

18.1.1 Symbols

°C	degrees Celsius
>	greater than
<	less than
%	percent

18.1.2 Alphabetical Characters

g	gram
L	liter
µg	microgram
mg	milligram
mg/L	milligram per liter
ml	milliliter
nm	nanometer

18.2 Definitions, acronyms, and abbreviations.

18.2.1 Analyte: CN, which is test for by this method.

18.2.2 Analytical bach: The set of samples analyzed at the same time, to a maximum of 20 samples. Each analytical batch must be accompanied by a laboratory blank (Section 9.4), and ongoing precision and recovery sample (OPR, Section 9.6), a matrix spike and matrix spike duplicate (MS/MSD, Section 9.3), and a reagent blank (Section 9.4).

18.2.3 CN: See Cyanide.

18.2.4 Cyanide (CN): The parameter which is tested for by this method.

18.2.5 CN Std Solution (CN^-): The standard solution from which the calibration and quality control samples can be prepared.

18.2.6 IPR: See initial precision and recovery.

18.2.7 Initial precision and recovery (IPR): Four aliquots of the diluted CN analyzed to establish the ability to generate acceptable precision and accuracy. An IPR is performed the first time this method is used and any time the method or instrument is modified.

18.2.8 Laboratory blank (method blank): An aliquot of reagent water that is treated exactly as a sample including exposure to all glassware, equipment, and reagents that are used with samples. The laboratory blank is used to determine if analyte or interferences are present in the laboratory environment, or the reagents.

18.2.9 Matrix spike (MS) and matrix spike duplicate (MSD): Aliquots of environmental sample to which known quantities of the analyte are added in the laboratory. The MS and MSD are prepared and/or analyzed exactly like a field sample. Their purpose is to quantify any additional bias and imprecision caused by the sample

matrix. The background concentration of the analyte in the sample matrix must be determined in a separate aliquot and the measured values in the MS and MSD corrected for background concentrations.

18.2.10 May: This action, activity, or procedural step is neither required nor prohibited.

18.2.11 May not: This action, activity, or procedural step is prohibited.

18.2.12 MemoChip: See transponder.

18.2.13 Merck Spectroquant® System Photometer: Photometer which can be used to perform the photometric measurements of the reacted Spectroquant® CN^- cell tests.

18.2.14 Method detection limit (MDL): The lowest level at which an analyte can be detected with 99 percent confidence that the analyte concentration is greater than zero.

18.2.15 Minimum level (ML): The lowest level at which the entire analytical system gives a recognizable signal and acceptable calibration point of the analyte. It is equivalent to the concentration of the lowest calibration standard, assuming that all method-specified sample weights, volumes, and preparation procedures have been employed.

18.2.16 Must: This action, activity, or procedural step is required.

18.2.17 OPR: See ongoing precision and recovery standard.

18.2.18 Ongoing precision and recovery standard (OPR): A laboratory blank spike with known quantities of analyte. The OPR is treated exactly like a sample. Its purpose is to establish performance of the method by the analyst.

18.2.19 Quality control sample (QCS): A sample containing analyte of interest at known concentrations. The QCS is obtained from a source external to the laboratory or is prepared from standards obtained from a different source than the calibration standards. The purpose is to check laboratory performance using test materials that heave been prepared independently from the normal preparation process.

18.2.20 Reagent water: Water demonstrated to be low or free from organic matter.

18.2.21 Shall: This action, activity, or procedural step is required.

18.2.22 Should: This action, activity, or procedural step is suggested, but not required.

18.2.23 Spectroquant® CN cell test: The pre-measured CN reagents, packaged in 16 x 100 mm tubes.

18.2.24 Transponder: The MemoChip, which contains updated information which may include new methods and updated calibration information for downloading into the Merck Spectroquant® system photometer.