METHOD 9014

CYANIDE IN WATERS AND EXTRACTS USING TITRIMETRIC AND MANUAL SPECTROPHOTOMETRIC PROCEDURES

SW-846 is not intended to be an analytical training manual. Therefore, method procedures are written based on the assumption that they will be followed by analysts who are formally trained in at least the basic principles of chemical analysis and in the use of the subject technology.

In addition, SW-846 methods, with the exception of required method use for the analysis of method-defined parameters, are intended to be guidance methods which contain general information on how to perform an analytical procedure or technique which a laboratory can use as a basic starting point for generating its own detailed standard operating procedure (SOP), either for its own general use or for a specific project application. The performance data included in this method are for guidance purposes only, and are not intended to be and must not be used as absolute QC acceptance criteria for purposes of laboratory accreditation.

1.0 SCOPE AND APPLICATION

1.1 This method can be used for measuring free (non-complexed) cyanide and hydrocyanic acid in drinking water, natural surface waters, domestic and industrial wastewaters, and in soil extracts. This method may also be used as a determinative step for quantifying total and amenable cyanide in the alkaline distillates from Method 9010.

1.2 The titration procedure of this method uses silver nitrate with *p*-dimethylaminobenzalrhodanine indicator and is used for measuring concentrations of cyanide exceeding 0.1 mg/L (0.025 mg/250 mL of absorbing liquid).

1.3 Prior to employing this method, analysts should consult the disclaimer statement at the front of the manual and the information in Chapter Two for guidance on the intended flexibility in the choice of methods, apparatus, materials, reagents, and supplies, and on the responsibilities of the analyst for demonstrating that the techniques employed are appropriate for the analytes of interest, in the matrix of interest, and at the levels of concern.

In addition, analysts and data users are advised that, except where explicitly required in a regulation, the use of SW-846 methods is *not* mandatory in response to Federal testing requirements. The information contained in this method is provided by EPA as guidance to be used by the analyst and the regulated community in making judgments necessary to generate results that meet the data quality objectives for the intended application.

1.4 This method is restricted to use by, or under supervision of, appropriately experienced and trained personnel. Each analyst must demonstrate the ability to generate acceptable results with this method.

2.0 SUMMARY OF METHOD

2.1 This method provides two options for the determination of cyanide; namely, a manual spectrophotometric (colorimetric) procedure or a titrimetric procedure.

2.2 In the colorimetric measurement, the cyanide is converted to cyanogen chloride (CNCl) by reaction of cyanide with chloramine-T at a pH less than 8. After the reaction is complete, color is formed on the addition of pyridine-barbituric acid reagent. The absorbance is read at 578 nm for the complex formed with pyridine-barbituric acid reagent and CNCl. To obtain colors of comparable intensity, it is essential to have the same salt content in both the sample and the standards.

2.3 The titration measurement uses a standard solution of silver nitrate to titrate cyanide in the presence of a silver sensitive indicator.

3.0 DEFINITIONS

Refer to Chapter One, Chapter Three, and the manufacturer's instructions for definitions that may be relevant to this procedure.

4.0 INTERFERENCES

4.1 Solvents, reagents, glassware, and other sample processing hardware may yield artifacts and/or interferences to sample analysis. All of these materials must be demonstrated to be free from interferences under the conditions of the analysis by analyzing method blanks. Specific selection of reagents and purification of solvents by distillation in all-glass systems may be necessary. Refer to each method to be used for specific guidance on quality control procedures and to Chapter Three for general guidance on the cleaning of glassware.

4.2 Interferences are eliminated or reduced by using the distillation procedure. Chlorine and sulfide are potential interferences in this method.

4.3 Oxidizing agents such as chlorine decompose most cyanides in solution. Chlorine interferences can be removed by adding an excess of sodium arsenite to the waste prior to preservation and storage of the sample to reduce the chlorine to chloride which does not interfere.

4.4 Sulfide interference can be removed by adding an excess of bismuth nitrate to the waste (to precipitate the sulfide) before distillation. Samples that contain hydrogen sulfide, metal sulfides, or other compounds that may produce hydrogen sulfide during the distillation should be treated by the addition of bismuth nitrate.

4.5 High results may be obtained for samples that contain nitrate and/or nitrite. During the distillation, nitrate and nitrite will form nitrous acid, which will react with some organic compounds to form oximes. These compounds, once formed, will decompose under test conditions to generate HCN. The possibility of interference of nitrate and nitrite is eliminated by pretreatment with sulfamic acid just before distillation. Nitrate and nitrite are interferences when present at levels higher than 10 mg/l and in conjunction with certain organic compounds.

4.6 Thiocyanate is reported to be an interferent when present at very high levels; levels of 10 mg/L or less were not found to interfere.

4.7 Fatty acids, detergents, surfactants, and other compounds may cause foaming during the distillation when they are present in high concentrations, and may make the endpoint for the titrimetric determination difficult to detect. They may be extracted at pH 6-7 to eliminate this interference.

5.0 SAFETY

5.1 This method does not address all safety issues associated with its use. 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.

WARNING: KCN and NaCN are highly toxic. Avoid skin and eye contact and inhalation.

5.2 Because of the toxicity of cyanide, exercise great care in its handling. Acidification of cyanide solutions produces lethal, toxic hydrogen cyanide (HCN) gas. Prepare all cyanide-containing solutions within a ventilation hood. Wear hand and eye protection at all times when working with cyanide.

6.0 EQUIPMENT AND SUPPLIES

The mention of trade names or commercial products in this manual is for illustrative purposes only, and does not constitute an EPA endorsement or exclusive recommendation for use. The products and instrument settings cited in SW-846 methods represent those products and settings used during method development or subsequently evaluated by the Agency. Glassware, reagents, supplies, equipment, and settings other than those listed in this manual may be employed provided that method performance appropriate for the intended application has been demonstrated and documented.

This section does not list all common laboratory glassware (e.g., beakers and flasks) that might be used.

6.1 Spectrophotometer - Suitable for measurements at 578 nm with a 1.0 cm cell or larger.

6.2 Hot plate stirrer/heating mantle.

6.3 pH meter.

6.4 Refrigerator.

6.5 5 mL microburette.

6.6 Class A volumetric flasks - 1000, 250, and 100 mL.

6.7 Erlenmeyer flask - 500 mL.

7.0 REAGENTS AND STANDARDS

7.1 Reagent-grade chemicals must be used in all tests. Unless otherwise indicated, it is intended that all reagents conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available. 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. Reagents should be stored in glass to prevent the leaching of contaminants from plastic containers. Note, however, that sodium hydroxide solutions of relatively moderate strength (i.e., 4.1 g/L and greater), should be stored in HDPE plastic containers whenever possible.

7.2 Reagent water -- Reagent water must be interference free. All references to water in this method refer to reagent water, unless otherwise specified.

7.3 Reagents for spectrophotometric determination

7.3.1 Sodium hydroxide solution (0.25N), NaOH - Dissolve 10 g of NaOH in 1 liter of water.

7.3.2 Sodium phosphate monobasic (1M), $NaH_2PO_4 \bullet H_2O$ - Dissolve 138 g of $NaH_2PO_4 \bullet H_2O$ in 1 liter of water. Refrigerate this solution.

7.3.3 Chloramine-T solution (0.44%), $C_7H_7ClNNaO_2S$ - Dissolve 1.0 g of white, water-soluble chloramine-T in 100 mL of water and refrigerate until ready to use.

7.3.4 Pyridine-barbituric acid reagent, $C_5H_5N \bullet C_4H_4N_2O_3$ - Place 15 g of barbituric acid in a 250-mL volumetric flask and add just enough water to wash the sides of the flask and wet the barbituric acid. Add 75 mL of pyridine and mix. Add 15 mL of concentrated hydrochloric acid (HCl), mix, and cool to room temperature. Dilute to 250 mL with water. This reagent is stable for approximately six months if stored in a cool, dark place.

7.3.5 Stock potassium cyanide solution (1 mL = 1000 μg CN^-), KCN - Dissolve 2.51 g of KCN and 2 g of KOH in 900 mL of water. Standardize with 0.0192N silver nitrate, $AgNO_3$. Dilute to appropriate concentration to achieve 1 mL = 1000 μg of CN^-.

NOTE: A detailed procedure for $AgNO_3$ standardization is described in Standard Methods for the Examination of Water and Wastewater, 18th Edition, 1992, "Method 4500-CN D."

7.3.6 Intermediate standard potassium cyanide solution (1 mL = 100 μg CN^-), KCN. Dilute 100 mL of stock potassium cyanide solution (1 mL = 1000 μg CN^-) to 1000 mL with water.

7.3.7 Working standard potassium cyanide solution (1 mL = 10 μg CN^-), KCN. Prepare fresh daily by diluting 100 mL of intermediate standard potassium cyanide solution and 10 mL of 1N NaOH to 1 liter with water.

7.4 Reagents for titration procedure

7.4.1 Rhodanine indicator - Dissolve 20 mg of p-dimethylamino-benzal-rhodanine, $C_{12}H_{12}N_2OS_2$, in 100 mL of acetone.

7.4.2 Standard silver nitrate solution (0.0192N), $AgNO_3$ - Prepare by crushing approximately 5 g of $AgNO_3$ and drying to constant weight at 40 °C. Weigh out 3.2647 g of

dried $AgNO_3$. Dissolve in 1 liter of water.

NOTE: A detailed procedure for $AgNO_3$ standardization is described in Standard Methods for the Examination of Water and Wastewater, 18th Edition, 1992, "Method 4500-CN D."

8.0 SAMPLE COLLECTION, PRESERVATION, AND STORAGE

Sample collection, preservation and storage requirements may vary by EPA program and may be specified in a regulation or project planning document that requires compliance monitoring for a given contaminant. Where such requirements are specified in the regulation, follow those requirements. In the absence of specific regulatory requirements, use the following information as guidance in determining the sample collection, preservation and storage requirements.

8.1 See the introductory material in Chapter Three, "Inorganic Analytes."

8.2 Samples should be collected in plastic or glass (preferably plastic) containers that are either amber or covered with aluminum foil so as to filter light at 400 nm and below and prevent photodecomposition of cyanide complexes. All containers must be thoroughly cleaned and rinsed prior to use. All sample containers must be prewashed with acids, water, and metal-free detergents, if necessary, depending on the use history of the container. For further information, see Chapter Three.

8.3 Aqueous samples for cyanide analysis should be preserved under alkaline conditions by adjusting the pH to 12 or greater using sodium hydroxide. Solid waste samples should be stored at $\leq$6 ºC after collection and prior to extraction.

8.4 Store all sample matrices at $\leq$6 ºC for no longer than 14 days. Solid phase samples must be extracted within 14 days of sample collection. Bring the samples to room temperature prior to analysis. Analysis of aqueous samples and solid phase extract solutions must be performed within 14 days of sample collection or extract generation.

8.5 Distillates that are not analyzed immediately should be stored in tightly sealed flasks at $\leq$6 °C.

9.0 QUALITY CONTROL

9.1 Refer to Chapter One for guidance on quality assurance (QA) and quality control (QC) protocols. When inconsistencies exist between QC guidelines, method-specific QC criteria take precedence over both technique-specific criteria and those criteria given in Chapter One, and technique-specific QC criteria take precedence over the criteria in Chapter One. Any effort involving the collection of analytical data should include development of a structured and systematic planning document, such as a Quality Assurance Project Plan (QAPP) or a Sampling and Analysis Plan (SAP), which translates project objectives and specifications into directions for those that will implement the project and assess the results. Each laboratory should maintain a formal quality assurance program. The laboratory should also maintain records to document the quality of the data generated. All data sheets and quality control data should be maintained for reference or inspection.

9.2 Initial demonstration of proficiency (IDP)

Prior to the analysis of samples an initial demonstration of method proficiency is accomplished through the successful calibration of method-specific instruments according to project requirements and criteria set forth in the applicable analytical methodology. This initial demonstration should be performed prior to independently running an analytical method, and should be repeated if other changes occur (e.g., instrument repair, significant change in procedure). Documentation of IDP should be maintained by the Quality Assurance Manager. The laboratory must also repeat the demonstration of proficiency whenever new staff members are trained or significant changes in instrumentation are made. See Method 8000 for information on how to accomplish an initial demonstration of proficiency.

An analytical instrument is said to be calibrated when an instrumental response can be related to the concentration of an analyte. This relationship may be depicted graphically, and referred to as a “calibration curve.” Initial calibration curves must be established based upon the requisite number of standards identified within the method for each target analyte (and surrogate for organic compounds). All reported concentrations for target analytes should be within the high and low initial calibration standards. Data generated above the high standard should be diluted into the calibration range and reanalyzed. The frequency requirements for the initial calibration vary among the individual methods.

Most analytical methods require multipoint (three or more) calibration that may include calibration blanks and higher levels so that unknowns fall within the calibration range and are bracketed by calibration points. The number of calibration points, the calibration range, and the frequency requirements should be specified in the QAPP.

9.3 Before processing any samples, the analyst should demonstrate that all parts of the equipment in contact with the sample and reagents are interference-free. This is accomplished through the analysis of a method blank. As a continuing check, each time samples are extracted, cleaned up, and analyzed, and when there is a change in reagents, a method blank should be prepared and analyzed for the compounds of interest as a safeguard against chronic laboratory contamination. If a measurable absorbance is observed at or in close proximity to the measurement wavelength of the target analyte that would prevent the accurate determination of that analyte, determine the source and eliminate it, if possible, before processing the samples. The blanks should be carried through all stages of sample preparation and analysis. When new reagents or chemicals are received, the laboratory should monitor the preparation and/or analysis blanks associated with samples for any signs of contamination. It is not necessary to test every new batch of reagents or chemicals prior to sample preparation if the source shows no prior problems. However, if reagents are changed during a preparation batch, separate blanks need to be prepared for each set of reagents.

The laboratory should not subtract the results of the method blank from those of any associated samples. Such "blank subtraction" may lead to negative sample results. If the method blank results do not meet the project-specific acceptance criteria and reanalysis is not practical, then the data user should be provided with the sample results, the method blank results, and a discussion of the corrective actions undertaken by the laboratory.

9.4 Sample quality control for preparation and analysis

The laboratory must also have procedures for documenting the effect of the matrix on method performance (precision, accuracy, method sensitivity). At a minimum, this should include the analysis of QC samples including a method blank, a matrix spike, a duplicate, and a laboratory control sample in each analytical batch. Any method blanks, matrix spike samples,

and replicate samples must be subjected to the same analytical procedures (Sec. 11.0) as those used on actual samples.

The following should be included within each analytical batch:

9.4.1 Method Blank - For each batch of samples analyzed, at least one method blank must be carried throughout the entire sample preparation and analytical process, including exposure to all glassware, equipment, solvents, filtration, and reagents that are used with field samples. Analysis of a method blank is used to assess contamination from the laboratory environment, equipment, and/or reagents. Any free cyanide measured in the method blank that exceeds the lower limit of quantitation (LLOQ) (Sec. 9.7) indicates that contamination is present. The source of the contamination should be determined and corrected prior to performing any sample analysis. Any sample included in an analysis batch that has an unacceptable method blank concentration should be reanalyzed in a subsequent batch after the contamination problem is resolved.

9.4.2 Matrix Spike (MS)/Duplicate - Documenting the effect of the matrix should include the analysis of at least one MS and one duplicate unspiked sample or one matrix spike/matrix spike duplicate (MS/MSD) pair. Both aqueous samples and solid sample extracts should be represented by a minimum of one MS sample for each respective matrix. The decision on whether to prepare and analyze duplicate samples or a MS/MSD must be based on knowledge of the samples in the sample batch. If samples are expected to contain the target analyte, laboratories may use a matrix spike (MS) and a duplicate analysis of an unspiked field sample. If samples are not expected to contain the target analyte, the laboratories should use a MS/MSD pair. Consult Method 8000 for information on developing acceptance criteria for the MS/MSD.

9.4.3 A laboratory control sample (LCS) should be included with each analytical batch. The LCS consists of an aliquot of a clean (control) matrix similar to the sample matrix and of the same weight or volume. The LCS is spiked with the same analytes at the same concentrations as the matrix spike, when appropriate. When the results of the matrix spike analysis indicate a potential problem due to the sample matrix itself, the LCS results are used to verify that the laboratory can perform the analysis in a clean matrix. Consult Method 8000 for information on developing acceptance criteria for the LCS.

9.4.4 Also see Method 8000 for the details on carrying out sample quality control procedures for preparation and analysis. In-house method performance criteria for evaluating method performance should be developed using the guidance found in Method 8000.

9.5 Initial Calibration Verification (ICV)

Immediately after the calibration standards have been analyzed, the accuracy of the calibration must be verified by the analysis of an ICV standard. The ICV is prepared in the same manner as a calibration standard (i.e., the sample is NOT processed through distillation) at a concentration level within the calibration range of the method and using a second source standard (prepared using standards different from the calibration standards) spiked into 0.25N sodium hydroxide (see Sec. 10.1). The control limit for the ICV is ±15% of the true value. When the ICV exceeds the control limits, the analysis should be terminated, the problem corrected, the instrument recalibrated, and the calibration re-verified.

9.6 Continuing Calibration Verification (CCV)

Once the calibration curve has been established, the continuing accuracy must be verified by analysis of a CCV after every tenth field sample, and at the end of the analysis sequence. The CCV is equivalent to or prepared in the same manner as a calibration standard (i.e., the sample is NOT processed through distillation) at a concentration level within the calibration range of the method and using the same source standard (prepared using the same source standards as those used to prepare the calibration standards) spiked into 0.25N sodium hydroxide (see Sec. 10.1). CCV concentrations alternating between the low- and mid-range calibration standard concentrations are recommended. The control limit for the low-range CCV is ± 50% and for the mid-range CCV is ± 15% of the true value. When the CCV exceeds the control limits, the analysis should be terminated, the problem corrected, the instrument recalibrated, and the calibration re-verified using an ICV analysis. Samples that are not bracketed by acceptable CCV runs must be reanalyzed.

9.7 Lower Limit of Quantitation (LLOQ) check standard

The laboratory should establish the LLOQ as the lowest point of quantitation which, in most cases, is the lowest concentration in the calibration curve. The LLOQ should be verified by the analysis of at least 7 replicate samples, spiked at the LLOQ and processed through all preparation and analysis steps of the method. The mean recovery and relative standard deviation of these samples provide an initial statement of precision and accuracy at the LLOQ. In most cases the mean recovery should be +/- 35% of the true value and RSD should be $\leq$ 20%. In-house limits may be calculated when sufficient data points exist.

9.7.1 The LLOQ verification is recommended for each project application or, at a minimum, on a quarterly basis to validate quantitation capability at low analyte concentration levels. This verification may be accomplished either with clean control material (e.g., reagent water, method blank, Ottawa sand, diatomaceous earth, etc.) or a representative sample matrix (free of target compounds). Optimally, the LLOQ should be less than or equal to the desired regulatory action levels based on the stated project-specific requirements.

9.7.1.1 The determination of LLOQs using spiked clean control material represents a best-case scenario, and does not evaluate the potential matrix effects of real-world samples. For the application of LLOQs on a project-specific basis, with established DQOs, a representative matrix-specific LLOQ verification may provide a more reliable estimate of the lower quantitation limit capabilities.

9.7.1.2 Alternatively, a representative sample matrix may be spiked with the analytes of interest at the predicted LLOQ concentration levels. This LLOQ check is carried through the same preparation procedures as the environmental samples and other QC. Individual LLOQs are verified when each respective analyte is recovered at ±50% of the predicted LLOQ concentration or established DQO criteria. This check may also be applied towards establishing the individual analyte reporting limit(s).

9.7.2 In-house limits may be calculated when sufficient data points exist.

9.8 It is recommended that the laboratory adopt additional QA practices for use with this method. The specific practices that are most productive depend upon the needs of the laboratory and the nature of the samples. Whenever possible, the laboratory should analyze standard reference materials and participate in relevant performance evaluation studies.

9.9 The method of standard additions must be used for the analysis of all samples that

suffer from matrix interferences such as samples which contain sulfides.

10.0 CALIBRATION AND STANDARDIZATION

10.1 Standard curve for samples without sulfide

10.1.1 Prepare a series of standards by pipetting suitable volumes of working standard potassium cyanide solution into 250-mL volumetric flasks. To each flask, add 50 mL of 1.25N sodium hydroxide and dilute to 250 mL with water. Prepare using the following table. The sodium hydroxide concentration will be 0.25N.

mL of Working Standard Solution (1 mL = 10 μg CN^-)	Concentration (μg CN^-/L)
0	Blank
1.0	40
2.0	80
5.0	200
10.0	400
15.0	600
20.0	800

10.1.2 After the standard solutions have been prepared according to the table above, pipet 50 mL of each standard solution into a 100-mL volumetric flask and proceed to Sections 11.2.2 and 11.2.3 to obtain absorbance values for the standard curve. The final concentrations for the standard curve will be one half of the amounts in the above table (final concentrations ranging from 20 to 400 μg/L).

10.1.3 Prepare a standard curve ranging from 20 to 400 μg/L by plotting absorbance of standard versus the cyanide concentration

10.2 Standard curve for samples with sulfide

10.2.1 It is imperative that all standards be distilled in the same manner as the samples using the method of standard additions. Standards distilled by this method will give a linear curve, at low concentrations, but as the concentration increases, the recovery decreases. It is recommended that at least five standards be distilled.

10.2.2 Prepare a series of standards similar in concentration to those mentioned in Sec. 10.1.1 and analyze as in Sec. 11.2. Prepare a standard curve by plotting absorbance of standard versus the cyanide concentration.

11.0 PROCEDURE

11.1 If the manual spectrophotometric determination will be performed, proceed to Sec. 11.2. If the titration procedure will be performed, proceed to Sec. 11.3.

11.2 Manual spectrophotometric (colorimetric) determination

11.2.1 Pipet 50 mL of sample or 50 mL of the scrubber solution obtained from the distillation procedure in Method 9010 into a 100-mL volumetric flask. If the sample is later found to be beyond the linear range of the colorimetric determination and redistillation of a smaller sample is not feasible, a smaller aliquot may be taken. If less than 50 mL is taken, dilute to 50 mL with 0.25N sodium hydroxide solution.

CAUTION: Temperature of reagents and spiking solution can affect the response factor of the colorimetric determination. The reagents stored in the refrigerator should be warmed to ambient temperature before use. Samples should not be left in a warm instrument to develop color, but instead they should be aliquoted to a cuvette immediately prior to reading the absorbance.

11.2.2 Add 15 mL of 1M sodium phosphate solution and mix. Add 2 mL of chloramine-T and mix. Some distillates may contain compounds that have chlorine demand. One minute after the addition of chloramine-T, test for excess chlorine with KI-starch paper. If the test is negative, add 0.5 mL chloramine-T. After 1 minute recheck with KI-starch paper. Continue to add chloramine-T in 0.5 mL increments until an excess is maintained. After 1 to 2 min., add 5 mL of pyridine-barbituric acid solution and mix.

11.2.3 Dilute to 100 mL with water and mix again. Allow 8 minutes for color development and then read the absorbance at 578 nm in a 1-cm cell within 15 min. The sodium hydroxide concentration will be 0.125N. See Sec. 10.0 for standard curves. See Sec. 12.1 for calculation.

11.2.4 See Sec. 10.0 for instructions regarding preparation of a standard curve based on whether the sample contains sulfides.

11.3 Titration procedure

11.3.1 Transfer the gas scrubber solution or a suitable aliquot from the 250-mL volumetric flask to a 500-mL Erlenmeyer flask. Add 10-12 drops of the rhodanine indicator.

11.3.2 Titrate with standard 0.0192N silver nitrate to the first change in color from yellow to brownish-pink. The titration must be performed slowly with constant stirring. Titrate a water blank using the same amount of sodium hydroxide and indicator used in the sample. The analyst should be familiar with the endpoint of the titration and the amount of indicator to be used before actually titrating the samples. A 5-mL burette may be conveniently used to obtain a precise titration.

NOTE: The titration is based on the following reaction:

$$Ag^{+} + 2CN \rightarrow [Ag(CN)_2]-$$

When all of the cyanide has complexed and more silver nitrate is added, the excess silver combines with the rhodanine indicator to turn the solution yellow and then brownish-pink. See Sec. 12.2 for calculation.

12.0 DATA ANALYSIS AND CALCULATIONS

12.1 If the spectrophotometric procedure is used, calculate the cyanide, in μg/L, in the

original sample as follows:

$$CN^- (\mu g/L) = \frac{A \times B \times C}{D \times E}$$

where:

A = μg/L CN^- read from standard curve.
B = mL of sample after preparation of colorimetric analysis (100 mL recommended).
C = mL of sample after distillation (250 mL recommended).
D = mL of original sample for distillation (500 mL recommended).
E = mL used for colorimetric analysis (50 mL recommended).

12.2 If the titrimetric procedure is used, calculate concentration of CN- in μg/L in the original sample as follows:

$$CN^-(\mu g/L) = \frac{(A-B)}{C} \times D \times \frac{E}{F} \times \frac{2\ mole\ CN^-}{1\ eq.\ AgNO_3} \times \frac{26.02\ g\ CN^-}{1\ mole\ CN^-} \times \frac{1 \times 10^6 \mu g}{1\ g}$$

where:

A = mL of $AgNO_3$ for titration of sample.
B = mL of $AgNO_3$ for titration of blank.
C = mL of sample titrated (250 mL recommended).
D = Actual normality of $AgNO_3$ (0.0192 N recommended).
E = mL of sample after distillation (250 mL recommended).
F = mL of original sample before distillation (500 mL recommended).

12.3 Results must be reported in units commensurate with their intended use and all dilutions must be taken into account when computing final results.

13.0 METHOD PERFORMANCE

13.1 Performance data and related information are provided in SW-846 methods only as examples and guidance. The data do not represent required performance goals for users of the methods. Instead, performance goals should be developed on a project-specific basis, and the laboratory should establish in-house QC performance criteria for the application of this method. These performance data are not intended to be and must not be used as absolute QC acceptance criteria for purposes of laboratory accreditation.

13.2 The titration procedure using silver nitrate is used for measuring concentrations of cyanide exceeding 0.1 mg/L. The colorimetric procedure is used for concentrations below 1 mg/L of cyanide and is sensitive to about 0.02 mg/L.

13.3 EPA Method 335.2 (sample distillation with titration) reports that in a single laboratory using mixed industrial and domestic waste samples at concentrations of 0.06 to 0.62 mg/L CN^-, the standard deviations for precision were ± 0.005 to ± 0.094, respectively. In a single laboratory using mixed industrial and domestic waste samples at concentrations of 0.28 and 0.62 mg/L CN^-, recoveries (accuracy) were 85% and 102%, respectively. These data are provided for guidance purposes only.

13.4 In two additional studies using surface water, ground water, and landfill leachate

samples, the titration procedure was further evaluated. The concentration range used in these studies was 0.5 to 10 mg/L cyanide. The detection limit was found to be 0.2 mg/L for both total and amenable cyanide determinations. The precision (CV) was 6.9 and 2.6 for total cyanide determinations and 18.6 and 9.1 for amenable cyanide determinations. The mean recoveries were 94% and 98.9% for total cyanide, and 86.7% and 97.4% for amenable cyanide. These data are provided for guidance purposes only.

14.0 POLLUTION PREVENTION

14.1 Pollution prevention encompasses any technique that reduces or eliminates the quantity and/or toxicity of waste at the point of generation. Numerous opportunities for pollution prevention exist in laboratory operation. The EPA has established a preferred hierarchy of environmental management techniques that places pollution prevention as the management option of first choice. Whenever feasible, laboratory personnel should use pollution prevention techniques to address their waste generation. When wastes cannot be feasibly reduced at the source, the Agency recommends recycling as the next best option.

14.2 For information about pollution prevention that may be applicable to laboratories and research institutions consult *Less is Better: Laboratory Chemical Management for Waste Reduction*, a free publication available from the American Chemical Society (ACS), Committee on Chemical Safety. http://portal.acs.org/portal/fileFetch/C/WPCP_012290/pdf/WPCP_012290.pdf

15.0 WASTE MANAGEMENT

The Environmental Protection Agency requires that laboratory waste management practices be conducted consistent with all applicable rules and regulations. 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, and by complying with all solid and hazardous waste regulations, particularly the hazardous waste identification rules and land disposal restrictions. For further information on waste management, consult the ACS publication listed in Sec. 14.2.

16.0 REFERENCES

There are no references directly related to this method. References on total and amenable cyanide can be found in Method 9010.

17.0 TABLES, DIAGRAMS, FLOWCHARTS, AND VALIDATION DATA

There are no tables or figures in this method.

Appendix A
Summary of Revisions to Method 9014 (from Revision 0, December 1996)

1. The entire document was updated to Microsoft Word .docx format from the original .WPD and .PDF files. The revision number was changed to one and the date published to July 2014.
2. Minor editorial and grammatical changes were made throughout the document, as needed.
3. Graphics in the Figures Section were modified from Corel Drawing Objects V.10 to .jpg graphical images (where needed) to remove artifacts from the conversion process. The text titles of each figure was centered and formatted.
4. Minor editorial comments from work group notes for 9013, 9014, 9015 in excel table were checked and were found to already be incorporated into the Method.
5. This appendix was added to document changes made during the editorial process.
6. The discussion of Initial Demonstration of Proficiency (IDP) in Section 9.2 was revised per language from Chapter One.
7. Significantly updated and expanded “QUALITY CONTROL” section for better adherence to current SW-846 method guidelines and for improved alignment with current universal practices for published analytical methods.
8. Inserted Section 9.7 to describe the use and application of LLOQ.