



Total Cyanide by Segmented Flow Injection Analysis, On-Line UV Digestion, and Amperometric Detection

(Cartridge Part #A001471, #A002654, #A002683)

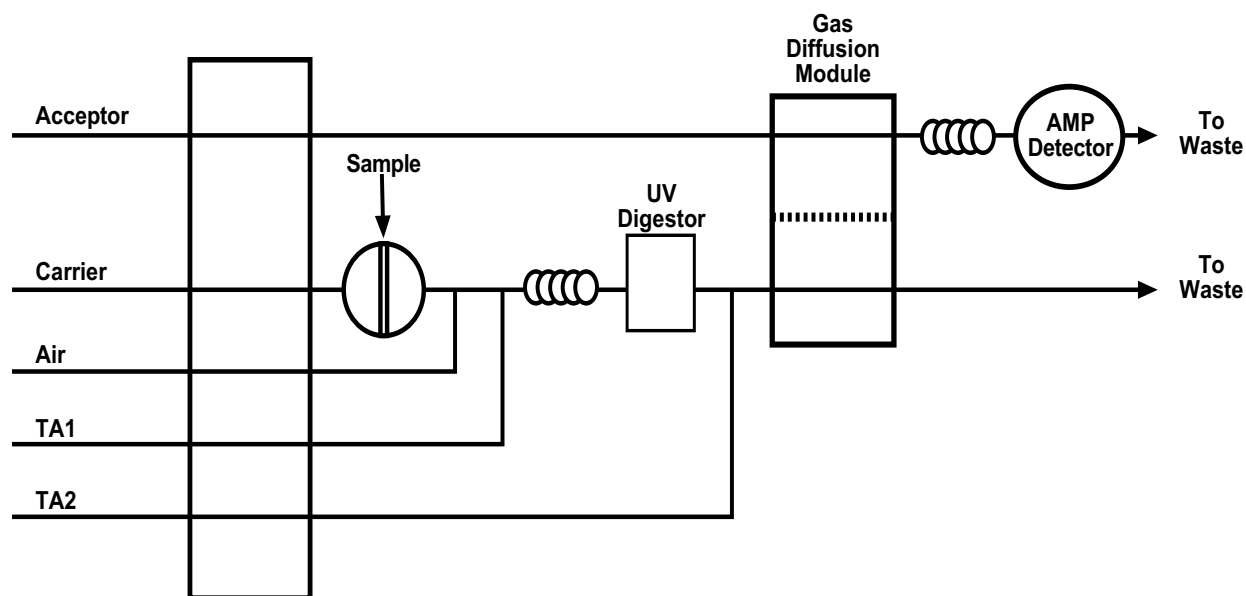
1.0 Scope and Application

- 1.1 This method is used for the determination of total cyanide in drinking and surface waters, as well as domestic and industrial wastes. Cyanide ion (CN^-), hydrogen cyanide in water ($\text{HCN}(\text{aq})$), and the cyano-complexes of zinc, copper, cadmium, mercury, nickel, silver, and iron may be determined by this method. Cyanide ions from $\text{Au}(\text{I})$, $\text{Co}(\text{III})$, $\text{Pd}(\text{II})$, and $\text{Ru}(\text{II})$ complexes are only partially determined.
- 1.2 The Method Detection Limit (MDL) of this method is 0.2 $\mu\text{g/L}$ cyanide. The applicable range is 2.0 $\mu\text{g/L}$ to 5.0 mg/L cyanide using a 200- μL sample loop. The range may be extended to analyze higher concentrations by sample dilution or by reducing the sample loop volume.

2.0 Summary of Method

- 2.1 Prior to analysis, the sample is pretreated to remove potential interferences (Sections 4.0 and 8.0). Cyanide is released from cyanide complexes by ultraviolet digestion. The addition of acid converts cyanide ion to hydrogen cyanide gas (HCN), which passes under a gas diffusion membrane. The hydrogen cyanide gas diffuses through the membrane into an alkaline receiving solution where it is converted back to cyanide ion. The cyanide ion is monitored amperometrically with a silver working electrode, silver/silver chloride reference electrode, and platinum/stainless steel counter electrode at an applied potential of zero volt. The current generated is proportional to the cyanide concentration present in the original sample.
- 2.2 The quality of the analysis is assured through reproducible calibration and testing of the Segmented Flow Injection Analysis (Segmented FIA) system.

- 2.3 A general flow diagram of the Segmented FIA system is shown below (see Section 17.0 for a detailed flow diagram).



3.0 Definitions

Definitions for terms used in this method are provided in Section 16.0, "Glossary of Definitions and Purposes."

4.0 Interferences

- 4.1 Method interferences may be caused by contaminants in the reagents, reagent water, glassware, etc., which may bias the results. Care should be taken to keep all such items free of contaminants.
- 4.2 Sulfide is a positive interferant in this method (References 15.2 and 15.3). When sulfide is acidified, it forms hydrogen sulfide, which passes through the gas diffusion membrane and produces a signal at the silver electrode. In addition, sulfide ion reacts with cyanide ion in solution to reduce its concentration over time. Samples containing sulfide must be treated according to Section 8.4. During the UV digestion some sulfur compounds may produce sulfide. In order to eliminate this potential interference, a sulfide scrubber that can remove up to 50 mg/L S^{2-} is added to the system prior to amperometric detection.
- 4.3 Sample containing water soluble aldehydes, such as formaldehyde or acetaldehyde, are treated by adding ethylenediamine solution (Section 8.5).
- 4.4 Oxidizing agents that decompose cyanides are removed by adding ascorbic acid (Section 8.6)
- 4.5 Thiocyanates produce a positive interference when they are decomposed to cyanide by ultraviolet radiation (References 15.5 and 15.7).

- 4.6 High concentrations of carbonate may result in a negative response in the amperometric detector when carbon dioxide diffuses across the gas diffusion membrane into the alkaline receiving solution, reducing its pH. Effluents from high-carbonate containing wastes, such as coal gasification wastes and atmospheric emission scrub waters, can be treated with hydrated lime to stabilize the sample (Reference 15.7).

5.0 Safety

- 5.1 The toxicity or carcinogenicity of each compound or reagent used in this method has not been fully established. Each chemical should be treated as a potential health hazard. Exposure to these chemicals should be reduced to the lowest possible level.
- 5.2 For reference purposes, a file of Material Safety Data Sheets (MSDS) for each chemical used in this method should be available to all personnel involved in this chemical analysis. The preparation of a formal safety plan is also advisable.
- 5.3 The following chemicals used in this method may be highly toxic or hazardous and should be handled with extreme caution at all times. Consult the appropriate MSDS before handling.
- 5.3.1 Acetic Acid, glacial, $C_2H_4O_2$ (FW 60.05)
- 5.3.2 Acetone, C_3H_6O (FW 58.08)
- 5.3.3 5-[4-(Dimethylamino)benzylidene]rhodanine, $C_{12}H_{12}N_2OS_2$ (FW 264.37)
- 5.3.4 Ethylenediamine, anhydrous, $C_2H_8N_2$ (FW 60.10)
- 5.3.5 Potassium Cyanide, KCN (FW 65.12)
- 5.3.6 Silver Nitrate, $AgNO_3$ (FW 169.88)
- 5.3.7 Sodium Acetate, anhydrous, $C_2H_3O_2Na$ (FW 82.03)
- 5.3.8 Sodium Hydroxide, NaOH (FW 40.00)
- 5.3.9 Total Acid 1 (TA 1) Reagent (Part #A001505)
- 5.3.10 Total Acid 2 (TA 2) Reagent (Part #A001872)
- 5.4 Unknown samples may be potentially hazardous and should be handled with extreme caution at all times.
- 5.5 Proper personal protective equipment (PPE) should be used when handling or working in the presence of chemicals.
- 5.6 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.

6.0 Apparatus, Equipment, and Supplies

- 6.1 Segmented Flow Injection Analysis (Segmented FIA) System (OI Analytical CNSolution™ 3000) consisting of the following:
 - 6.1.1 120-Place Autosampler
 - 6.1.2 Amperometric detection system with:
 - 6.1.2.1 Silver working electrode
 - 6.1.2.2 Silver/silver chloride reference electrode
 - 6.1.2.3 Platinum/stainless steel counter electrode
 - 6.1.2.4 Applied potential of zero volt
 - 6.1.3 Data Acquisition System (PC or Notebook PC) with WinFLOW™ software
 - 6.1.4 Total Cyanide by UV Digestion Cartridge (Part #A001471, #A002654, or #A002683)
- 6.2 Sampling equipment—Sample bottle, amber glass, with polytetrafluoroethylene (PTFE)-lined cap. Clean by washing with detergent and water, rinsing with two aliquots of reagent water, and drying by baking at 110°–150°C for a minimum of one hour.
- 6.3 Standard laboratory equipment including volumetric flasks, pipettes, syringes, etc. should all be cleaned, rinsed, and dried per bottle cleaning procedure in Section 6.2.

7.0 Reagents and Calibrants

- 7.1 Raw Materials
 - 7.1.1 Acetic Acid, glacial, $C_2H_4O_2$ (FW 60.05)
 - 7.1.2 Acetone, C_3H_6O (FW 58.08)
 - 7.1.3 Ascorbic Acid, $C_6H_8O_6$ (FW 176.12)
 - 7.1.4 Brij®-35, 30% w/v (Part #A21-0110-33)
 - 7.1.5 Deionized Water (ASTM Type I or II)
 - 7.1.6 5-[4-(Dimethylamino)benzylidene]rhodanine, $C_{12}H_{12}N_2OS_2$ (FW 264.37)
 - 7.1.7 Ethylenediamine, anhydrous, $C_2H_8N_2$ (FW 60.10)
 - 7.1.8 Potassium Cyanide, KCN (FW 65.12)

7.1.9 Silver Nitrate, AgNO_3 (FW 169.88)

7.1.10 Sodium Acetate, anhydrous, $\text{C}_2\text{H}_3\text{O}_2\text{Na}$ (FW 82.03)

7.1.11 Sodium Hydroxide, NaOH (FW 40.00)

7.1.12 Total Acid 1 (TA 1) Reagent (Part #A001505)

7.1.13 Total Acid 2 (TA 2) Reagent (Part #A001872)

7.2 Reagent Preparation

Note: For best results, filter and degas all reagents prior to use.

7.2.1 Reagent Water

7.2.1.1 Degassed and deionized reagent water can be prepared in one of the following manners:

7.2.1.1.1 Place distilled/deionized water under a strong vacuum for 15–20 minutes. Magnetic stirring or sonification will aid in the degassing process.

7.2.1.1.2 Purge distilled/deionized water with a stream of nitrogen gas (or other inert gas) through a glass frit for approximately 5 minutes.

7.2.1.1.3 Boil distilled/deionized water in an Erlenmeyer flask for 15–20 minutes. Remove the flask from the heat source, cover it with an inverted beaker, and allow it to cool to room temperature.

7.2.1.2 After preparing the degassed reagent water, store the reagent water in a tightly sealed container to protect it from reabsorption of atmospheric gases. For best results, store degassed reagent water under a slight vacuum when not in use.

7.2.2 Sample Preservation Reagents

7.2.2.1 Acetate Buffer (1 L)

7.2.2.1.1 Dissolve 146 g of sodium acetate anhydrous in 400 mL of reagent water (Section 7.2.1).

7.2.2.1.2 Add 480 g of glacial acetic acid. Dilute to 1,000 mL with reagent water in a 1-L volumetric flask and mix well.

7.2.2.2 Ethylenediamine Solution, 3.5% v/v (100 mL)

7.2.2.2.1 Dilute 3.5 mL of ethylenediamine to 100 mL with reagent water in a 100-mL volumetric flask and mix well.

7.2.2.3 Ascorbic Acid—Crystals

7.2.3 Segmented FIA Reagents

7.2.3.1 Start-up and Carrier Solution, 0.1% v/v Brij-35 (1 L)

7.2.3.1.1 Dilute 3.5 mL of Brij-35 with reagent water to 1,000 mL in a 1-L volumetric flask and mix well.

7.2.3.2 Acceptor Stock Solution, 5 M Sodium Hydroxide (1 L)

7.2.3.2.1 While stirring, carefully add 200 g of sodium hydroxide in 700 mL of reagent water in a 1-L volumetric flask.

7.2.3.2.2 Cool to room temperature. Dilute to 1,000 mL with reagent water and mix well.

Warning: Mixing sodium hydroxide with water releases a great amount of heat. Take appropriate precautions, such as cooling the solution while adding the sodium hydroxide.

Note: Store in an amber bottle at room temperature.

7.2.3.3 Acceptor Reagent, 0.1 M Sodium Hydroxide (1 L)

7.2.3.3.1 Dilute 20 mL of acceptor stock solution with reagent water to 1,000 mL in a 1-L volumetric flask and mix well).

Note: Store in an amber bottle at room temperature.

7.2.3.4 Total Acid 1 (TA 1) Reagent (Part #A001505)

7.2.3.5 Total Acid 2 (TA 2) Reagent (Part #A001872)

7.3 Calibrant Preparation

7.3.1 Stock Solutions

7.3.1.1 Silver Nitrate Solution, 0.0192 N (1 L)

7.3.1.1.1 Dissolve 3.27 g of silver nitrate in 700 mL of reagent water in a 1-L volumetric flask.

7.3.1.1.2 Dilute to 1,000 mL with reagent water and mix well.

Note: Store in an amber bottle at room temperature.

7.3.1.2 Rhodanine Solution, 0.2 mg/mL in Acetone (100 mL)

7.3.1.2.1 Dissolve 20 mg of 5-[4-(dimethylamino)benzylidene]rhodanine in 80 mL of acetone in a 100-mL volumetric flask.

7.3.1.2.2 Dilute to 100 mL with acetone and mix well.

7.3.1.3 Potassium Cyanide Stock Solution, 1,000 mg/mL (1 L)

7.3.1.3.1 Dissolve 2 g of sodium hydroxide in 500 mL of reagent water in a 1-L volumetric flask.

7.3.1.3.2 Add 2.51 g of potassium cyanide. Dilute to 1,000 mL with reagent water and mix well.

Warning: Mixing sodium hydroxide with water releases a great amount of heat. Take appropriate precautions, such as cooling the solution while adding the sodium hydroxide.

Warning: Cyanide ion, hydrocyanic acid, all cyanide salts, and most metal-cyanide complexes are extremely dangerous. As a contact poison, cyanide need not be ingested to produce toxicity. Also, cyanide solutions produce fatally toxic hydrogen cyanide gas when acidified. For these reasons, it is mandatory that work with cyanide be carried out in a well-ventilated hood by properly trained personnel wearing adequate protective equipment.

Note: Store in an amber bottle at 4°C. If stored properly, this reagent is typically stable for two months.

7.3.1.4 Standardized Potassium Cyanide Stock Solution

7.3.1.4.1 Add 0.5 mL of rhodanine solution (Section 7.3.1.2) to 25 mL of potassium cyanide stock solution (Section 7.3.1.3).

7.3.1.4.2 Titrate with silver nitrate solution (Section 7.3.1.1) until the color changes from canary yellow to a salmon hue.

7.3.1.4.3 Based on the determined potassium cyanide concentration, dilute the potassium cyanide stock solution to the final concentration of 1.00 g/L using Equation 1. If the concentration is not 1.00 g/L, correct the intermediate and working calibration concentrations accordingly.

Note: Store in an amber bottle at 4°C. If stored properly, this reagent is typically stable for two months.

EQUATION 1

$$xV_1 = CV_2$$

Where:

x = Concentration of potassium cyanide stock solution determined from titrations

C = 1.00 g/L potassium cyanide

V_1 = Volume (in L) of potassium cyanide stock solution needed to prepare 1 L of 1.00 g/L standardized potassium cyanide stock solution

V_2 = 1 L, final volume (in L) of standardized potassium cyanide stock solution

7.3.1.5 Sodium Hydroxide, 1 M (1 L)

7.3.1.5.1 While stirring, carefully add 40 g of sodium hydroxide in 700 mL of reagent water in a 1-L volumetric flask.

7.3.1.5.2 Cool to room temperature. Dilute to 1,000 mL with reagent water and mix well.

Warning: Mixing sodium hydroxide with water releases a great amount of heat. Take appropriate precautions, such as cooling the solution while adding the sodium hydroxide.

Note: Store in an amber bottle at room temperature.

7.3.2 Secondary Calibrants

7.3.2.1 Cyanide, 100 mg/L (1 L)

7.3.2.1.1 Add 100 mL of standardized potassium cyanide stock solution (Section 7.3.1.4) and 10 mL of 1 M sodium hydroxide (Section 7.3.1.5) to a 1-L volumetric flask.

7.3.2.1.2 Dilute to 1,000 mL with reagent water and mix well.

Note: Store in an amber bottle at 4°C. If stored properly, this reagent is typically stable for 2–4 weeks.

7.3.2.2 Cyanide, 10 mg/L (1 L)

7.3.2.2.1 Use a volumetric pipet to add 10 mL of standardized potassium cyanide stock solution and 10 mL of 1 M sodium hydroxide to a 1-L volumetric flask.

7.3.2.2.2 Dilute to 1,000 mL with reagent water and mix well.

Note: Store in an amber bottle at 4°C. If stored properly, this reagent is typically stable for 2–4 weeks.

7.3.2.3 Cyanide, 1 mg/L (1 L)

7.3.2.3.1 Use a volumetric pipet to add 1.0 mL of standardized potassium cyanide stock solution and 1 mL of 1 M sodium hydroxide to a 1-L volumetric flask.

7.3.2.3.2 Dilute to 1,000 mL with reagent water and mix well.

Note: Store in an amber bottle at 4°C. If stored properly, this reagent is typically stable for 2–4 weeks.

7.3.3 Working Calibrants

7.3.3.1 Add the designated volumes of secondary calibrant (see Equation 2) to the required number of 100-mL volumetric flasks that each contain approximately 40 mL of reagent water.

7.3.3.2 Dilute each solution to the mark with reagent water and mix well.

Note: Prepare working calibrants fresh daily.

EQUATION 2

$$C_1 V_1 = C_2 V_2$$

Where:

C_1 = Concentration (in mg/L) of stock solution (or calibrant)

V_1 = Volume (in L) of stock solution (or calibrant) to be used

C_2 = Desired concentration (in mg/L) of working calibrant to be prepared

V_2 = Final volume (in L) of working calibrant to be prepared

By solving this equation for the volume of stock solution to be used (V_1), the following equation is obtained:

$$V_1 = \frac{C_2 V_2}{C_1}$$

Since the desired concentration (C_2), the final volume (V_2), and the concentration of the stock solution (C_1) are all known for any given calibrant concentration in a defined volume, the volume of stock solution to be used (V_1) is easily calculated.

7.3.3.3 Calibrants covering the entire range of this analysis can be prepared from the following table.

Working Calibrant Final Concentration (µg/L)	Volume of Secondary Calibrant Solution (mL)		
	Cyanide 1 mg/L	Cyanide 10 mg/L	Cyanide 100 mg/L
1.0	0.10		
2.0	0.20		
5.0	0.50	0.05	
10	1.0	0.10	
50	5.0	0.50	0.05
100	10	1.0	0.10
200	20	2.0	0.20
500	50	5.0	0.50
1,000		10	1.0
3,000		30	3.0
5,000		50	5.0

8.0 Sample Collection, Preservation, and Storage

- 8.1 Samples should be collected in plastic or glass bottles that have been thoroughly cleaned and rinsed with reagent water (Section 7.2.1).
- 8.2 The volume of sample collected should be sufficient to ensure that a representative sample is obtained, replicate analysis is possible, and waste disposal is minimized.
- 8.3 Determine cyanide in unpreserved samples within 24 hours or as soon as possible to eliminate loss of analyte.
- 8.4 Samples Containing Sulfide Ion
 - 8.4.1 Sulfide ion should be precipitated with lead ion immediately upon sample collection. Sulfide ion and lead sulfide will react with cyanide ion to form thiocyanate, which is not detected in the analytical system. If lead carbonate is used for sulfide precipitation, the supernate containing cyanide must be filtered immediately to avoid loss of cyanide through reaction with precipitated lead sulfide (Reference 15.8).
 - 8.4.2 Samples can be tested with lead acetate test paper to determine the presence or absence of sulfide ion. Note that the lead acetate test paper can be unreliable and is typically not usable for sulfide concentrations below approximately 1 ppm. If the presence of sulfide is suspected but not verifiable by the 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 unpreserved sample. Lead acetate test paper should be tested for minimum level of sulfide detection by spiking reagent water aliquots with decreasing levels of sulfide. The spiked samples are tested with lead acetate test paper moistened with acetate buffer (Section 7.2.2.1). 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.
- 8.5 Treat samples containing or suspected to contain formaldehyde, acetaldehyde, or other water soluble aldehydes with 20 mL of 3.5% ethylenediamine solution (Section 7.2.2.2) per liter of sample.
- 8.6 Treat samples containing chlorine, hypochlorite, and/or sulfite with 0.6 g of ascorbic acid per liter of sample.
- 8.7 Treat samples containing high concentrations of carbonate with hydrated lime.
 - 8.7.1 Slowly add hydrated lime while stirring to raise the pH of the sample to 12.0–12.5.
 - 8.7.2 Decant the sample after the precipitate has settled.
- 8.8 The holding time for preserved samples is 14 days from the time of collection (Reference 15.6). Sample analysis should be performed as soon as possible to eliminate loss of analyte.

9.0 Quality Control

Note: The following QC procedures are provided for reference purposes only and are not a substitute for any QC procedures that may be required for regulatory compliance.

- 9.1 It is recommended that each laboratory that uses this method operate a formal quality control program. The minimum requirements of such a program should consist of an initial demonstration of laboratory capability and the periodic analysis of Laboratory Control Samples (LCSs) and Matrix Spike/Matrix Spike Duplicates (MS/MSDs) as a continuing check on performance. Laboratory performance should be compared to established performance criteria to determine if the results of the analyses meet the performance characteristics of the method.
- 9.2 Method Detection Limit (MDL)—To establish the ability to detect cyanide at low levels, the analyst should determine the MDL using the apparatus, reagents, and calibrants that will be used in the practice of this method. An MDL less than or equal to the MDL listed in Section 1.2 should be achieved prior to practice of this method.
- 9.2.1 An MDL is calculated by analyzing a matrix spike at a concentration of two to three times the expected detection limit of the analyzer. Seven consecutive replicate analyses of this matrix spike should be analyzed, and the MDL should be calculated using Equation 3.

EQUATION 3

$$MDL = (t) \times (S)$$

Where:

t = Student's t value for a 99% confidence level and a standard deviation estimate with n–1 degrees of freedom (t = 3.14 for seven replicates)

S = Standard deviation of the replicate analyses

- 9.2.2 It is recommended that the MDL be calculated after every six months of operation, when a new operator begins work, or whenever there is any significant change in the instrument response.
- 9.3 Analyses of MS/MSD samples are required to demonstrate method accuracy and precision and to monitor matrix interferences (interferences caused by the sample matrix).
- 9.3.1 Matrix Spike/Matrix Spike Duplicate (MS/MSD)—The laboratory should spike, in duplicate, a minimum of 10% of all samples (one sample in duplicate in each batch of 10 samples) from a given sampling site.
- 9.3.2 The concentration of the spike in the sample shall be determined as follows:

- 9.3.2.1 If, as in compliance monitoring, the concentration of cyanide in the sample is being checked against a regulatory concentration limit, the spiking level shall be at that limit.
- 9.3.2.2 If the concentration of cyanide in a sample is not being checked against a limit, the spike shall be at the concentration of the LCS or at least four times greater than the MDL.
- 9.4 Analyses of Laboratory Reagent Blanks (LRBs) are required to demonstrate freedom from contamination and that the compounds of interest and interfering compounds have not been carried over from a previous analysis.
- 9.5 As part of the QC program for the laboratory, method precision and accuracy for samples should be assessed and records should be maintained.
 - 9.5.1 An LCS should be analyzed with every sample batch, and the mean (m) and the standard deviation (S) should be recorded. After multiple analyses, the mean should be plotted with limits of $m+2S$ and $m-2S$. The mean and the limits should be recalculated after every 5–10 new measurements.
 - 9.5.2 If the LCS measurement falls outside the range calculated in Section 9.5.1, then the problem should be addressed, and that sample batch should be reanalyzed if necessary.
- 9.6 Reference Sample—To demonstrate that the analytical system is in control, the laboratory may wish to periodically test an external reference sample, such as a Standard Reference Material (SRM) available from the National Institute of Standards and Technology (NIST). Corrective action should be taken if the measured concentration significantly differs from the stated concentration.

10.0 Configuration and Start-up

10.1 Instrument Configuration

- 10.1.1 Configure the OI Analytical CNSolution 3000 Analyzer according to the Operator's Manual (Reference 15.1) and verify that each module is properly powered on.
- 10.1.2 Verify that the Total Cyanide by UV Digestion Cartridge (Part #A001471, #A002654, or #A002683) is configured as illustrated in the flow diagram shown in Section 17.0.
- 10.1.3 Connect the appropriate pump tubes to the cartridge and to their reagent containers according to the flow diagram.

10.2 Instrument Stabilization

- 10.2.1 Start the pump, allowing the reagents to flow through the entire system.

- 10.2.2 Verify that the flowcell of each detector is purged of all bubbles and the flow is stable and free from surging.
- 10.2.3 Load a 10 mg/L cyanide calibrant into the sampling valve and inject it into the Segmented FIA system.
- 10.2.4 Continue to inject 10 mg/L cyanide calibrant until three successive peak heights or area results are within 5% RSD, indicating that the electrode system is stabilized.
- 10.2.5 Following stabilization, inject the highest concentration calibration standard until three successive peak heights or area results are within 5% RSD, indicating stabilization at the top of the calibration range.

10.3 Baseline Verification

- 10.3.1 Create and save a Method in WinFLOW. Refer to the WinFLOW Operator's Manual (Reference 15.9) for help on creating a Method.
- 10.3.2 Create and save a Sample Table in WinFLOW that will be used to generate a calibration curve using at least three calibrants that cover the full range of expected concentrations in the samples to be analyzed. This Sample Table should also be used to analyze all necessary QC samples as well as the analytical batch of samples to be analyzed. For help on creating a Sample Table, refer to the WinFLOW Operator's Manual (Reference 15.9).
- 10.3.3 Select **Collect Data** in the WinFLOW main window, enter the user's identification, select the appropriate Method and Sample Table, and begin to collect baseline data. Very sharp fluctuations in the baseline and/or consistent drifting are typically signs of bubbles in the flowcell. The flowcell must be free of bubbles prior to beginning analysis.

10.4 Calibration and Standardization

- 10.4.1 Prepare a series of at least three working calibrants using the stock solutions (Section 7.3.3) according to Equation 2, covering the desired analysis range.
- 10.4.2 Place the calibrants in the autosampler in order of decreasing concentration. Each calibrant should be analyzed according to the analytical procedures in Section 11.0. A calibration curve will be calculated by the WinFLOW software.
- 10.4.3 Acceptance or control limits for the calibration results should be established using the difference between the measured value of each calibrant and the corresponding "true" concentration.
- 10.4.4 Each calibration curve should be verified by analysis of a Laboratory Control Sample (LCS, Section 9.5). Using WinFLOW software, calibration, verification, and sample analysis may be performed in one continuous analysis.

11.0 Procedure

11.1 Analysis

11.1.1 Begin pump flow with the start-up solution (Section 7.2.3.1) and verify a stable baseline (Section 10.3).

11.1.2 Place all reagents on-line and allow to pump at least 10–15 minutes and verify there are no bubbles in the flowcell. Obtain a stable baseline and autozero the baseline before beginning analysis.

11.1.3 Load the sampler tray with calibrants, blanks, samples, and QC samples.

Note: The matrix of the working standards, blanks, and QC samples should match that of the samples being analyzed.

11.1.4 Using the Method and Sample Table created for the analytical batch to be analyzed and with the baseline verified to be stable, begin the analysis by selecting the “Fast Forward” button on the left side of the Data Analysis window in WinFLOW. This will initiate the sequential analysis of samples as defined in the Sample Table.

11.1.5 When analysis is complete, pump start-up solution through the system for at least 10–15 minutes. Stop the pump, release the tension on all pump tubes, and power off the system.

11.2 Operating Notes

11.2.1 If the sample is composed of 100% Fe(III) cyanide complex, the sample should be diluted to a concentration below 1 mg/L to insure recoveries of at least 90%. Above 1 mg/L, recovery of less than 90% is expected for Fe(III) cyanide complexes.

12.0 Data Analysis and Calculations

12.1 The calibration curve allows for accurate quantitation of the concentration in each sample.

12.2 WinFLOW software reports the concentration of each sample relative to the calibration curve.

13.0 Method Performance

Range:	2.0 µg/L–5.0 mg/L
Throughput:	30 samples/hour
Precision:	
2.0 µg/L	<2% RSD
5.0 mg/L	<0.5% RSD
Method Detection Limit (MDL):	0.2 µg/L

14.0 Pollution Prevention and Waste Management

- 14.1 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 restrictions. In addition, it is the laboratory's responsibility to protect air, water, and land resources by minimizing and controlling all releases from fume hoods and bench operations. Also, compliance is required with any sewage discharge permits and regulations.
- 14.2 Samples containing cyanide, certain metals and acids at a pH of less than two are hazardous and must be treated before being poured down a drain or must be handled as hazardous waste.
- 14.3 For further information on waste management, consult Section 13.6 of *Less is Better: Laboratory Chemical Management for Waste Reduction* (Reference 15.4).

15.0 References

- 15.1 CNSolution 3000 Operator's Manual. Available from OI Analytical, Box 9010, College Station, TX, 77842-9010.
- 15.2 *Code of Federal Regulations*, Part 136, Appendix B, Title 40, 1994.
- 15.3 Ingersol, D.; Harris, W.R.; Bomberger, D.C.; Coulson, D.M. *Development and Evaluation Procedures for the Analysis of Simple Cyanides, Total Cyanides, and Thiocyanate in Water and Waste Water*: 1983; EPA-600/4-83-054; Environmental Protection Agency, Environmental Monitoring Systems Laboratory, U.S. Government Printing Office: Washington, DC, 1983.
- 15.4 *Less is Better: Laboratory Chemical Management for Waste Reduction*. Available from the American Chemical Society, Department of Government Regulations and Science Policy, 1155 16th Street, NW, Washington, DC, 20036.
- 15.5 Cyanide. *Methods for Chemical Analysis of Water and Wastewater*; EPA-600/4-79-020; U.S. Environmental Protection Agency, Office of Research and Development, Environmental Monitoring and Support Laboratory: Cincinnati, OH, 1984; Method 335.3.
- 15.6 Sample Preservation. *Methods for Chemical Analysis of Water and Wastes*; EPA-600/4-79-020; U.S. Environmental Protection Agency, Office of Research and Development, Environmental Monitoring and Support Laboratory: Cincinnati, OH, 1984; xvii.
- 15.7 *Standard Methods for the Examination of Water and Wastewater*, 17th ed.; American Public Health Association: Washington, D.C., 1989; 4–178.
- 15.8 Wilmont, J.C.; Solujic, L.; Milosavljevic, E.B.; Hendrix, J.L.; Rader, W.S. Formation of Thiocyanate During Removal of Sulfide as Lead Sulfide Prior to Cyanide Determination. *Analyst* **1996**, 121, 799-801.
- 15.9 WinFLOW Software and Operator's Manual (Part #A002877). Available from OI Analytical, P.O. Box 9010, College Station, TX, 77842-9010.

16.0 Glossary of Definitions and Purposes

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

16.1 Units of weights and measures and their abbreviations

16.1.1 Symbols

°C	degrees Celsius
%	percent
±	plus or minus
≥	greater than or equal to
≤	less than or equal to

16.1.2 Alphabetical characters

g	gram
L	liter
mg	milligram
mg/L	milligram per liter
µg	microgram
µg/L	microgram per liter
mL	milliliter
ppm	parts per million
ppb	parts per billion
M	molar solution
N	normal solution

16.2 Definitions

16.2.1 Initial Precision and Recovery (IPR)—Four aliquots of the LRB spiked with the analytes of interest and used 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 instrumentation is modified.

16.2.2 Laboratory Control Sample (LCS)—An aliquot of LRB to which a quantity of the analyte of interest is added in the laboratory. The LCS is analyzed like a sample. Its purpose is to determine whether the methodology is in control and whether the laboratory is capable of making accurate and precise measurements.

16.2.3 Laboratory Reagent Blank (LRB)—An aliquot of reagent water and other blank matrix that is treated like a sample, including exposure to all glassware, equipment, and reagents that are used with other samples. The LRB is used to determine if the method analyte or other interferences are present in the laboratory environment, reagents, or apparatus.

- 16.2.4 Matrix Spike/Matrix Spike Duplicate (MS/MSD)—An aliquot of an environmental sample to which a quantity of the method analyte is added in the laboratory. The MS/MSD is analyzed like a sample. Its purpose is to determine whether the sample matrix contributes bias to the analytical results. The background concentration of the analyte in the sample matrix must be determined in a separate aliquot, and the measured values in the MS/MSD must be corrected for the background concentration.
- 16.2.5 Method Detection Limit (MDL)—The minimum concentration of a substance that can be measured and reported with 99% confidence that the analyte concentration is greater than zero.
- 16.2.6 Minimum Level (ML)—The level at which the entire analytical system will give a recognizable signal and acceptable calibration point, taking into account method-specific sample and injection volumes.
- 16.2.7 Ongoing Precision and Recovery (OPR)—See Section 16.2.2, “Laboratory Control Sample.”

17.0 Figures

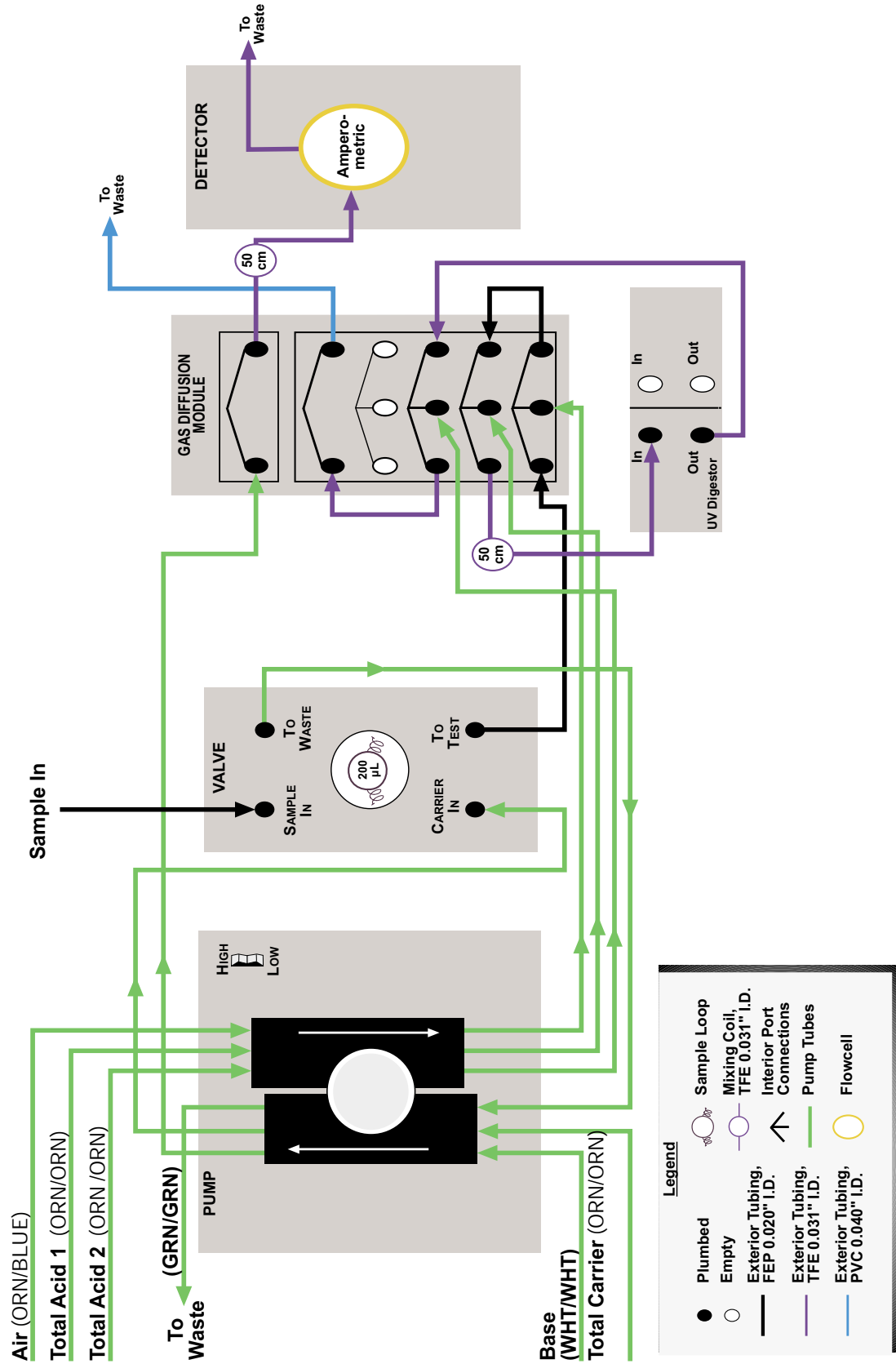


Figure 1. Detailed Flow Diagram for Total Cyanide by Segmented FIA on a CNSolution 3000, Cartridge Part #A001471, A002654 or A002683

Results were obtained under optimal operating conditions. Actual results may vary depending on sample introduction, cleanliness of sample containers, reagent purity, operator skill, and maintenance of instruments.

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