METHOD 9016

FREE CYANIDE IN WATER, SOILS AND SOLID WASTES BY MICRODIFFUSION

SW-846 is not intended to be an analytical training manual. Therefore, method procedures are written based on the assumption that they will be performed 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 test method covers the determination of free cyanide in waste waters, ground waters, surface waters, drinking waters, soils and solid wastes. This test method reports the cyanide that dissociates from simple cyanides or weakly-bound metal cyanide complexes (Sec. 3.0) at room temperature, from a solution of pH 6-6.5 (Ref. 1). The following analyte has been determined by this method:

Analyte	CAS No.[a]
CN^-	57-12-5

[a]Chemical Abstract Service Registry Number

1.2 This test method does not determine strongly-bound metal cyanide complexes that resist dissociation, such as the hexacyanoferrates and gold cyanide, nor does it determine thiocyanate and cyanohydrin.

1.3 Prior to employing this method, analysts are advised to consult the base method for each type of procedure that may be employed in the overall analysis (e.g., Method 9014) for additional information on quality control (QC) procedures, development of QC acceptance criteria, calculations, and general guidance. Analysts also 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 specified 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, properly experienced and trained personnel. Each analyst must demonstrate the ability to generate acceptable results with this method.

2.0 SUMMARY OF METHOD

2.1 The sample preparation (Sec. 11.2) is carried out using a microdiffusion cell (Figure 1 and Figure 2) (Ref. 2). The water, wastewater or extract sample is introduced in the outer chamber of the microdiffusion cell and is buffered at pH 6 and placed in the dark for 6 hrs of diffusion. The free cyanide diffuses as HCN gas and is absorbed as CN^- into the sodium hydroxide solution located in the center chamber of the microdiffusion cell.

2.2 An aliquot of the sodium hydroxide absorber solution is removed and treated with acidified phosphate buffer and chloramine-T to convert the CN^- to cyanogen chloride. The cyanogen chloride is reacted with pyridine-barbituric acid to form a color complex that absorbs at 578 to 587 nm. The free cyanide is determined spectrophotometrically by measuring the absorbance of the sample and determining the concentration through comparison with a standard calibration curve (Sec. 11.3).

2.3 Solids are first extracted prior to analysis using pH 12.3-12.5 NaOH solution (Sec. 11.1). The filtered extracts are then diffused (Sec. 11.2) and analyzed spectrophotometrically as described in Sec. 11.3. The extraction conditions described in this method have been found to be effective at extracting free cyanide from a variety of solid wastes. Figure 3 illustrates the effects of various extraction conditions on the recovery of free cyanide in a complex, mixed-waste sample.

The extraction conditions in this method may be modified as needed to improve free cyanide extraction efficiency from other matrices. For example, certain relatively complicated wastes or waste mixtures may not yield acceptable matrix spike recoveries. In such cases, additional refinement of the extraction step and/or the use of chemical pretreatments may be necessary to improve free cyanide recovery. Such flexibility is allowed as long as the data meets the quality objectives of the specific project.

3.0 DEFINITIONS

Refer to Chapter One, Chapter Three, and the manufacturer's instructions for definitions that may be relevant to this procedure. In addition, the following standard terms have been established to describe the most commonly-found, aqueous-phase cyanide species. See Ref. 3 for more detailed information.

3.1 Free cyanide — Cyanide ion (CN^-) or hydrogen cyanide (HCN), the distribution of which depends on the pH of the sample solution (pK_{HCN} = 9.24; Ref. 4) (see Figure 4).

3.2 Simple cyanide — A neutral compound comprised of an alkali metal, alkaline earth metal or ammonium cation bound to free cyanide. Simple cyanides are so named because of their structural simplicity and their ability to completely dissociate in water to produce free cyanide and a free metal or ammonium cation.

3.3 Metal cyanide complex — A negatively-charged ionic complex consisting of several cyanide ions bound to a single transition metal cation.

3.4 Total cyanide — The sum total of all of the inorganic chemical forms of cyanide. Total cyanide thus may include free cyanide, simple cyanide, and anionic metal cyanide complexes.

4.0 INTERFERENCES

4.1 Interferences, such as chlorine and sulfides, can degrade samples by reacting with the free cyanide present. All aqueous samples should be checked at the time of their collection to determine the presence of oxidizing agents and/or sulfides. If found to be present, the samples should be immediately treated, as noted in the following sections, prior to their storage for future analysis.

4.1.2 Oxidizing agents, such as chlorine, decompose free cyanide. Chlorine reacts with free cyanide to form cyanogen chloride (CNCl), which under alkaline conditions hydrolyzes to cyanate (CNO^-). Chlorine interferences can be removed by adding excess amounts of sodium arsenite or sodium thiosulfate to the sample prior to storage. Both sodium arsenite and sodium thiosulfate reduce the chlorine to chloride, which does not react with free cyanide or otherwise interfere in its analysis (see Sec. 8.4).

4.1.2 Sulfide oxidation products can rapidly convert free cyanide to thiocyanate (SCN^-), especially at high pH (Refs. 4 and 5). Sulfide interferences (namely hydrogen sulfide, metal sulfides, or other compounds that may produce sulfide) can be removed by adding an excess of either lead carbonate or lead acetate to the sample. The addition of either reagent forms insoluble lead sulfide (PbS), so that it may be removed via filtration, prior to storage or analysis (see Sec. 8.5).

4.2 Volatility losses of free cyanide (as HCN) can occur in samples having pH values less than 12. If samples cannot be analyzed immediately after field collection and treatment for oxidizing agents and sulfides, they must be preserved by adjusting the pH to 12 or greater prior to storage.

4.3 In addition to oxidizing agents and sulfides, free cyanide can react with other chemicals such as aldehydes. Because of the reactivity of free cyanide, it is important that analysis is completed as soon as possible after sample collection. It is beyond the scope of this method to list all the possible cyanide reactions that may be encountered.

4.4 Hexacyanoferrate complexes in water samples can decompose when exposed to UV light (Refs.3 and 5) and produce free cyanide. This decomposition is virtually eliminated during the test procedure by allowing samples to diffuse in the dark.

4.5 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 QC procedures and to Chapter Three for general guidance on the cleaning of glassware. Also, refer to the Method 9014 for additional discussion of interferences.

5.0 SAFETY

5.1 This method does not address all safety issues associated with its use. The laboratory and analyst is responsible for maintaining a safe work environment and a current awareness file of OSHA regulations regarding the safe handling of the chemicals listed 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 toxic gaseous hydrogen cyanide (HCN). Perform all manipulations in the hood so that any HCN gas that is formed is safely vented.

5.3 Some of the reagents used in these methods, such as those containing cyanide and pyridine-barbituric acid solutions, are highly toxic in the environment. Dispose of such reagents and their solutions properly, according to applicable state or local regulations.

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 common laboratory glassware (e.g., beakers and flasks).

6.1 Supplies/equipment for sample collection, preservation, and handling

6.1.1 Potassium iodide-starch test paper.

6.1.2 Lead-acetate paper test paper

6.1.3 pH test paper

6.1.4 Plastic conway-type microdiffusion cell*, 83-mm OD — Equipped with a fitted lid or other type cover, for use in maintaining an airtight seal when in place (Sec. 11.2.3); manufactured by Bel-Art or other commercial vendor

6.2 Additional supplies/equipment for extraction of solid samples

6.2.1 Extraction bottles, HDPE, 1000-mL capacity or larger

6.2.2 Agitation apparatus — Rotary agitator (provides end-over-end motion), orbital shaker or rotary shaker or other equivalent apparatus, capable of providing thorough mixing of samples during extraction.

6.3 Supplies/equipment for microdiffusion processing (Sec. 11.2) and spectrophotometric analysis (Sec. 11.3)

6.3.1 Micropipets, 0.20-mL, 0.50-mL, 1.00-mL, 1.50-mL, 2.50-mL, 5.00-mL, 10.0-mL, 15.0-mL, and 30.0-mL

6.3.2 Adjustable pipet or calibrated syringe — Able to be adjusted to deliver exactly 3.00 mL of solution

6.3.3 Adjustable pipet or calibrated syringe — Able to be adjusted to deliver exactly 1.30 mL of solution

6.3.4 Spectrophotometer — Suitable for making absorbance measurements between 575 and 590 nm using a 1.0-cm cell

6.3.5 Spectrophotometer cell, 1-cm — equipped with a fitted stopper

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

* Fisher Scientific is a supplier of microdiffusion cells suitable for this procedure.

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.

NOTE: The preparation of smaller volumes of standards and reagents is recommended, whenever feasible, in order to minimize the amount of hazardous waste generated during execution of this method.

7.2 Reagent water — Reagent water must be interference-free. All references to water in this method refer to reagent water, as defined in Chapter One of SW-846 manual.

7.3 Reagents for sample collection, preservation, and handling

7.3.1 Sodium arsenite, $NaAsO_2$

7.3.2 Sodium thiosulfate, $Na_2S_2O_3$

7.3.3 Lead acetate trihydrate, $Pb(CH_3COO)_2 \cdot 3H_2O$

7.3.4 Lead carbonate, $PbCO_3$.

7.3.5 Sodium hydroxide solution (50% w/w; ρ = 1.53 g/mL), NaOH; commercially-prepared.

7.4 Additional reagents needed for extraction of solid samples

7.4.1 Sodium hydroxide solution (50% w/w) (see Sec. 7.3.5)

7.4.2 Sodium hydroxide extraction solution (pH 12.3-12.5) — Weigh either 2.53 g or measure 1.65 mL of 50% sodium hydroxide solution and transfer to a 1-L volumetric flask containing approximately 800 mL of reagent water. Stir until dissolved. Adjust the final volume to 1-L using reagent water. Using pH test paper, check to ensure that the extraction solution is in the proper pH range. Add additional 50% NaOH, if necessary, to adjust the pH to the proper range.

7.5 Additional reagents needed for microdiffusion processing (Sec. 11.2) and spectrophotometric analysis (Sec. 11.3).

7.5.1 Sodium hydroxide solution (2.05 g/L), NaOH — Weigh either 4.10 g or measure 2.68 mL of 50% sodium hydroxide solution and transfer to a 1-L volumetric flask containing approximately 800 mL reagent water. Stir until dissolved. Cool the solution to room temperature and adjust the final volume to 1 L using reagent water. This solution is used only for the preparation of initial demonstration of proficiency samples, method blanks, matrix spikes and laboratory control standards.

7.5.2 Sodium hydroxide solution (4.1 g/L) — Weigh either 8.20 g or measure 5.36 mL of 50% sodium hydroxide solution and transfer to a 1-L volumetric flask containing approximately 800 mL of reagent water. Stir until dissolved. Adjust the final volume to 1-L using reagent water.

CAUTION: Calibration standards are commercially available from several sources including Supelco, AccuStandard and Radian, as both solutions and neat materials. It is **highly recommended** that commercially-prepared stock standard solutions be obtained rather than the handling of neat materials.

7.5.3 Potassium cyanide, KCN; or sodium cyanide, NaCN

7.5.4 Stock cyanide standard (1000 mg/L) — Add 500 mL of 4.1-g/L sodium hydroxide solution contained to a 1-L volumetric flask. Dissolve in either 2.51 g of potassium cyanide or 1.89 g of sodium cyanide. Dilute solution to 500 mL using additional 4.1-g/L sodium hydroxide.

NOTE: The stock cyanide solution must be standardized to determine the exact concentration of cyanide. This standardization is carried out via silver-nitrate titration, using *p*-dimethylaminobenzalrhodanine for titration endpoint indication. Re-standardize the solution weekly. Refer to Method 9014 for instructions on titration standardization of the stock cyanide solution.

7.5.5 Standard cyanide solution (2 mg/L) — Pipet 2.00 mL of 1000-mg/L stock cyanide solution into a 1-L volumetric flask and dilute to volume using 4.1-g/L sodium hydroxide solution. This solution is used in the preparation of calibration standards (see Sec. 10.1).

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

7.5.6 Stopcock grease, petroleum jelly or mineral oil; to help in providing an air-tight seal between the microdiffusion cell and lid

7.5.7 Potassium phosphate monobasic, KH_2PO_4

7.5.8 Sodium hydroxide solution (100 g/L), NaOH — Weigh either 200 g or measure 131 mL of 50% sodium hydroxide solution and transfer to a 1-L volumetric flask containing approximately 800 mL reagent water. Stir until dissolved. Cool the solution to room temperature and adjust the final volume to 1 L using reagent water.

7.5.9 Concentrated phosphoric acid (sp gr 1.69), H_3PO_4

7.5.10 Potassium phosphate solution (190 g/L) — Add 400 mL of reagent water to a 2-L beaker. Next, either weigh 29 g or measure 19 mL of 50%-sodium hydroxide solution, transfer to beaker, and dissolve. Add 190 g of potassium phosphate monobasic and stir to dissolve. Bring the volume to approximately

950-mL to aid in dissolution. Adjust the pH of the solution so that it is within the range of 5.9-6.1, using 100-g/L sodium hydroxide or concentrated phosphoric acid. Transfer the solution to a 1-L volumetric flask, and dilute to volume with reagent water.

7.5.11 Potassium phosphate buffer solution (acidified) — Add 8.0 mL of concentrated phosphoric acid to 100 mL of 190-g/L potassium phosphate solution.

7.5.12 Chloramine-T reagent (10 g/L) — Dissolve 1.0 g of chloramine-T in 50 mL of reagent water contained in a 100-mL volumetric flask. Dilute to volume with additional reagent water. Prepare fresh daily.

7.5.13 Barbituric acid, $NHCONHCOCH_2CO$

7.5.14 Pyridine, C_5H_5N

7.5.15 Concentrated hydrochloric acid (sp gr 1.19), HCl

7.5.16 Pyridine-barbituric acid reagent — Add 15.0 g of barbituric acid to a 250-mL volumetric flask. Wash down the sides of the flask with just enough reagent water to moisten the barbituric acid. Add 75 mL of pyridine and swirl to mix. Slowly, add 15 mL of concentrated hydrochloric acid and swirl to mix. Using additional reagent water, bring volume to approximately 230 mL. Stir to dissolve and cool the solution to room temperature. Dilute to final volume with additional reagent water and mix. It is recommended that the reagent be prepared fresh weekly and stored in a dark place. Discard and prepare a new batch if a precipitate develops.

WARNING: Pyridine is toxic; avoid contact or inhalation. Prepare this reagent in an exhaust hood.

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 All samples must be collected using a sampling plan that addresses the considerations discussed in Chapter Nine of the SW-846 manual.

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 metal 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 A single, satisfactory preservation technique is not available for samples containing free cyanide. Reactions between free cyanide and oxidizing agents, sulfides and aldehydes will occur. The following procedural steps are strongly recommended in order to inhibit analyte degradation reactions that may take place.

8.4 Testing and treatment for oxidizing agents

8.4.1 All samples whose origin or composition is not well-known should be tested for the presence or absence of oxidizing agents, such as chlorine, ideally at the time of sample collection.

8.4.2 Place a drop of sample on a strip of potassium iodide-starch test paper. A bluish discoloration of the test paper indicates the presence of oxidizing agents. If this occurs, add sodium arsenite (approximately, 0.1 g $NaAsO_2$/L sample).

8.4.3 Continue testing the sample for the presence of oxidizing agents, making repeat additions of sodium arsenite, as needed, until all oxidizing agents have been treated (as evidenced by a lack of color change on the test paper).

NOTE: Sodium thiosulfate may be used instead of sodium arsenite, but it should not be added in excess of 0.1 g/L sample.

8.5 Testing and treatment for sulfides

8.5.1 All samples whose origin or composition is not well-known should be tested for the presence or absence of sulfides, ideally just following collection and testing/pretreatment for oxidizing agents (Sec. 8.4).

8.5.2 Place a drop of sample on a strip of lead-acetate test paper. Darkening of the test paper indicates the presence of sulfides. If this occurs, add sodium arsenite (approximately, 0.1 g $NaAsO_2$/L sample).

8.5.3 Continue testing the sample for sulfides, making repeat additions of sodium arsenite (Sec. 8.5.2), as needed, until all sulfides have been treated (as verified when the test paper no longer darkens).

NOTE: If the sulfide concentration appears to be too high, powdered lead carbonate should be substituted for sodium arsenite in order to avoid significantly lowering the sample pH.

8.5.4 Filter the sample to remove any precipitated lead sulfate.

8.6 Analyze samples immediately; otherwise preserve them at the time of collection, following any treatment for oxidizing agents (Sec. 8.4) or sulfides (Sec. 8.5), by adding 50% sodium hydroxide, until the pH is equal to or slightly greater than 12. This minimizes cyanide losses due to volatilization of HCN.

8.7 Store properly-preserved samples in the dark at 4 $\pm$ 2 °C.

8.8 When properly preserved, cyanide samples can be stored for up to 14 days prior to analysis.

8.9 Extract solids within 14 days of sample collection.

8.10 Analyze extracts of solid samples within 24 hrs following extraction.

9.0 QUALITY CONTROL

9.1 Refer to Chapter One for guidance on quality assurance (QA) and 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 QA 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)

Each laboratory must demonstrate initial proficiency with each sample preparation and determinative method combination it utilizes by generating data of acceptable accuracy and precision for the target analyte in a clean matrix. 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.

NOTE: The free cyanide IDP samples should be prepared in 2.05 g/L sodium hydroxide (see Sec. 7.5.1).

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 A method blank (MB) is prepared from a 2.05 g/L sodium hydroxide solution and treated exactly as a field sample, including exposure to all glassware, equipment, solvents, filtration, and reagents that are used with field samples. Analysis of an MB is used to assess contamination from the laboratory environment, equipment, and/or reagents. Any free cyanide measured in the MB that exceeds the lower limit of quantitation (LLOQ) (Sec. 9.8) 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 MB concentration should be reanalyzed in a subsequent batch after the contamination problem is resolved.

9.4.2 Documenting the effect of the matrix should include the analysis of at least one matrix spike (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 a 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.

NOTE: **Spiking immediately prior to microdiffusion processing is of critical importance when preparing MSs of extracts from solid samples.** This is because soils and related solid wastes typically contain relatively large levels of free transition metals, which can potentially form complexes with the spiked free cyanide, resulting in low spike recovery values.

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.

NOTE: The free cyanide LCS sample should be prepared in 2.05 g/L sodium hydroxide (see Sec. 7.5.1).

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 the microdiffusion procedure) 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 4.1 g/L 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 the microdiffusion procedure) 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 4.1 g/L 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 verification is recommended for each project application 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 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.

9.7.1.1 A matrix-free LLOQ check standard is prepared by spiking a clean control material with the analyte(s) of interest at the predicted LLOQ concentration level(s). This LLOQ check is carried through the same preparation procedures as the environmental samples and other QC. Recovery should be ±50% (or other such project-required acceptance limits for accuracy and precision) of the true value to verify the data reporting limits(s). The low-range CCV standard (Sec. 9.6), if prepared at the appropriate concentration, may also serve as the LLOQ verification for confirming method sensitivity.

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.

10.0 CALIBRATION AND STANDARDIZATION

10.1 Preparation of calibration standards - Pipet 0, 0.20, 0.50, 1.00, 2.50, 5.00, 10.0, 15.0, and 30 mL of the 2.0-mg/L cyanide standard solution (Sec. 7.5.5) into nine separate 200-mL volumetric flasks. Dilute each of the flasks to volume with 4.1-g/L sodium hydroxide solution. These dilutions yield calibration standards that contain approximately 0, 2.0, 5.0, 10, 25, 50, 100, 150, and 300 µg/L cyanide, respectively. Additional calibration standards may be added if desired.

NOTE: The 0 µg/L cyanide standard sample is used as the calibration blank.

10.2 To establish the calibration curve, analyze the calibration standards in accordance with the procedure in Section 11.2. This is accomplished by carrying out color development and spectrophotometric analysis on a 1.00 mL aliquot of standard as described in Secs. 11.2.1-11.2.7. Prepare a duplicate set of spectrophotometric samples for each respective calibration standard (Sec. 10.1) to provide for duplicate spectrophotometric analyses of each standard. In order to avoid a method bias, the calibration standards must be analyzed directly and not processed through the microdiffusion procedure (Section 11.1).

10.3 Calculate the average absorbance reading for each duplicate set of calibration standards analyzed.

10.4 Establish the calibration curve by plotting average absorbance versus cyanide concentration. An example of a calibration curve is presented in Figure 5. A new calibration curve should be established daily with each analysis. Perform a first-order linear regression of the calibration curve (i.e., $y = ax + b$ function). The acceptance criterion for the calibration curve should be a correlation coefficient of 0.995 or higher.

10.5 Verify the accuracy of the initial calibration curve as described in Sec. 9.4.

11.0 PROCEDURE

CAUTION: This method requires manual dexterity, practice, and meticulous attention to operational consistency. Best practices are noted throughout this section to assist analysts in achieving optimum results. Adherence to these practices is highly recommended for attaining precise and accurate data.

NOTE: Observe the specified time periods in the procedural steps where such is noted. Establish provisions so as to guarantee that all spectrophotometric measurements are able to be completed in the 3-6-min time interval recommended in the procedure (See Sec.11.3)

NOTE: Store all samples in the dark whenever possible during processing. Light of 400 nm and under can dissociate metal cyanide complexes, thus yielding artificially-high free cyanide values.

11.1 Extraction of free cyanide from solid samples

Extract solid samples prior to microdiffusion and analysis, otherwise proceed to Sec. 11.2.

11.1.1 Weigh 250 mg $PbCO_3$ and transfer to an extraction bottle.

NOTE: Since, sulfides are often present in soils and solid wastes, lead carbonate is added to all extract samples in order to fix sulfides as PbS.

11.1.2 Weigh a 1 g sample of the solid to be analyzed, recording the sample mass to 0.001 g. Transfer the weighed sample to the extraction bottle containing the lead carbonate.

11.1.3 Add 500 mL of pH 12.3-12.5–NaOH solution to the extraction bottle and gently rotate the bottle so as to mix the contents.

11.1.4 Cap the extraction bottle, place on agitation apparatus and agitate for 5 min. After 5 min, use a strip of pH test paper check the sample mixture pH to verify that it is within the range of 12.3-12.5. If it is not, add 50% NaOH drop-wise, to bring the pH to within the proper range. Recap the bottle and restart agitation. Extract the free cyanide in this manner for a period of 60 min.

11.1.5 At the end of the extraction period, use a strip of pH test paper to verify that the sample mixture pH is 11 or greater. If the pH is in the correct range, the extraction may be deemed to be acceptable – proceed to Sec. 11.1.6. If it is not, extract a new sample by repeating Secs. 11.1.1-11.1.5, except using an initially higher-pH extraction solution (e.g., pH 13)

11.1.6 Following a successful extraction, decant the sample supernatant into a clean container. Filter the supernatant through a 0.45 µm membrane filter to remove particulate material and any PbS that may have formed.

11.1.7 If necessary, centrifuge the extraction mixture at 5,000 rpm for 20 min, or other such velocity and time, as needed to remove fine particles and afford an adequate separation, as evidenced by a relatively clear final extract solution.

11.2 Microdiffusion of free cyanide in aqueous samples and extracts

NOTE: At a minimum, perform microdiffusion of all samples in duplicate. More diffusion replicates can be performed, if desired, for greater statistical confidence in the final result.

11.2.1 Using a pipet or calibrated syringe, dispense 3.00 mL of sample into the outer chamber of a clean, dry microdiffusion cell (see Figure 2).

11.2.2 Using an adjustable pipet or calibrated syringe, dispense exactly 1.30 mL of 4.1-g/L sodium hydroxide solution into the center chamber of the microdiffusion cell (see Figure 2).

11.2.3 Smear the microdiffusion cell lid or other such cover with a sufficiently heavy layer of stopcock grease or petroleum jelly to prepare for airtight sealing of the microdiffusion cell, which occurs later in the test procedure. The most appropriate manner in which to apply the grease depends on the construction and geometry of the microdiffusion cell. In some cases a better air-tight seal may be achieved by applying the grease directly to the cell, instead of the lid. Either practice is considered to be acceptable.

NOTE: Use a liberal amount of stopcock grease or petroleum jelly in order to create an airtight seal between the microdiffusion cell and the lid.

11.2.4 Using a calibrated syringe (or pipet), immediately inject 1.0 mL of 190-g/L potassium phosphate solution into the sample located in the outer chamber of the microdiffusion cell. Inject at an angle in order to force the solution around the chamber.

NOTE: The force of ejection of aids in the proper mixing of the solutions.

11.2.5 Perform this step as quickly and carefully as possible in order to avoid loss of free cyanide: Carefully tilt and rotate the cell once to mix the constituents and immediately, use pH test paper to check the sample and ensure that it has attained a pH of 6. If the sample pH is greater than 6, add additional 190-g/L potassium phosphate solution, using 1.0-1.5 mL, increments, as necessary, to adjust the sample pH to 6.

NOTE: When analyzing an unknown sample, it is strongly recommended that the sample be pre-tested prior to microdiffusion analysis in order to determine the exact amount of potassium phosphate solution needed to adjust the sample pH to 6. This may be accomplished by pipetting 3.0 mL of sample into a small container (e.g., volume capacity of 10 mL) followed by addition of 1.0 mL of 190-g/L potassium phosphate solution. After mixing the solutions well, determine the amount of potassium phosphate solution required to attain a pH of 6.

NOTE: The pH measurement step in Sec. 11.2.5 may be eliminated based upon historical knowledge of the sample.

11.2.6 Quickly, seal the cell by fitting it with a greased lid (Sec. 11.2.3). Twist the lid and microdiffusion cell back and forth to ensure that the grease is evenly spread between the cell and the lid for an airtight seal.

11.2.7 Carefully tilt and rotate the cell for 5 seconds to ensure proper mixing.

NOTE: Exercise great care during mixing of solutions by tilting and rotating the microdiffusion cell carefully so as to avoid spilling or splashing the contents from one chamber of the cell to the other.

11.2.8 Place the covered cell in the dark at room temperature for a period of 6 hr.

NOTE: It is essential that the microdiffusion cell be protected from light at all times during the 6-hr diffusion period in order to avoid photolysis of hexacyanoferrate complexes.

11.2.9 Proceed to analyze the diffused samples and standards as described in Sec. 11.3.

11.3 Color development and spectrophotometric analysis of diffused samples and standards

NOTE: Ensure that the spectrophotometer cells used for analysis are optically-matched prior to use.

11.3.1 Prepare the spectrophotometer for analysis according to the manufacturer's instructions.

11.3.2 Set the spectrophotometer wavelength to 578 nm or other optimum wavelength, as determined by this method (See Section 11.2).

11.3.3 When the instrument has stabilized, zero the detector against the 4.1-g/L sodium hydroxide solution.

11.3.4 At the end of the diffusion period, pipet a 1.00-mL aliquot of the sodium hydroxide solution from the center chamber of the microdiffusion cell and dispense into a clean, dry, spectrophotometer cell.

CAUTION: Complete mixing as indicated in each of the following steps (Secs. 11.3.5-11.3.7) is critical for accurate analysis.

11.3.5 Using a micropipet, dispense 0.1 mL of acidified potassium phosphate buffer into the spectrophotometer cell. Seal the cell with the stopper. The stopper should form a watertight seal. While holding the stopper tightly against the cell, invert the cell 4-5 times to mix.

NOTE: Some spectrophotometer cell lids do not fit tightly and as such, mixing the cell contents through inversion can result in leaking and sample loss. A small piece of Parafilm M® may be used in place of the spectrophotometer stopper to provide a better seal and prevent leakage.

NOTE: In order to provide for more thorough mixing and at the same time prevent sample loss, Steps 11.3.4-11.3.7 may be carried out in a test tube instead of a spectrophotometer cell. After each addition of reagent, the sample test

tube is vortexed (using a Vortex mixer) to stir the contents. Prior to spectrophotometric analysis (Sec. 11.3.8) the contents from the test tube are transferred to a clean, dry spectrophotometric cell.

11.3.6 Dispense 0.50 mL of chloramine-T reagent into the spectrophotometer cell using a micropipet. Seal the cell tightly again with the stopper and invert 4-5 times to mix.

11.3.7 Pipet 1.00 mL of pyridine-barbituric acid reagent into the spectrophotometer cell and replace the stopper. Note the time (Sec. 11.3.8) and invert the cell 8-10 times to mix.

11.3.8 Within 3-6 min from the start of mixing (Sec. 11.3.7), the development of the color complex, as well as its stability, will be optimum for performing spectrophotometric readings. Read the absorbance of the spectrophotometric sample at 578 nm during this time interval. The time interval at which readings are taken must be consistent to the extent possible for all samples and standards.

NOTE: The wavelength maximum of the color-complex can vary slightly with each bottle or lot of barbituric acid reagent due solvatochromic effects. For optimum results, the absorbance maximum for the color complex can be determined by performing a spectral scan of a prepared 150-µg/L calibration standard prior to analysis each day. The sample and calibration standard absorbance readings may then be measured at the determined wavelength maximum, instead of at 578 nm.

11.3.9 Measure the absorbance for each sample replicate. Average the replicate results to yield a single absorbance value for each sample.

NOTE: The cells can be cleaned between usages by rinsing well with reagent water, followed by methanol. For a large number of determinations (10 or more), it may be necessary to periodically clean the cells with chromic-sulfuric acid cleaning solution or methanol-hydrochloric acid solution (prepare by mixing 3 volumes of water, 1 volume of concentrated HCl and 4 volumes of methanol). Avoid contact of these reagents with skin or eyes. Methanol may be used to dry the cell afterwards, if necessary.

WARNING: Keep any methanol used for cleaning purposes away from ignition sources.

NOTE: The total volume of liquid in the spectrophotometer cell is 2.6 mL. This is normally sufficient for measuring the absorbance in most spectrophotometers. However, if a larger cell is used and/or a greater sample volume is needed, the volume of acidified potassium phosphate buffer added to the sample (Section 11.3.5) may be increased, as long as it is performed consistently for other samples and calibration standards.

12.0 DATA ANALYSIS AND CALCULATIONS

12.1 For each spectrophotometric sample, obtain the µg/L free cyanide concentration from the calibration curve established in Sec. 10.4.

12.2 Determine the actual free cyanide concentration in an aqueous (or solid extract) sample by mathematically adjusting the free cyanide concentration determined in Sec. 12.1 to account for the concentration effect of the microdiffusion process as follows:

$$\frac{\mu g}{L} \text{ free } CN^- \text{ in aqueous sample} =$$

$$\frac{1.3 \text{ mL (center chamber solution volume)}}{3.0 \text{ mL (outer chamber solution volume)}} \times \frac{\mu g}{L} \text{ free } CN^- \text{ in spectrophotometric sample}$$

NOTE: Samples having a free cyanide concentration that exceeds that of the highest calibration standard, as determined in Sec. 12.1, must be diluted appropriately and reanalyzed spectrophotometrically (Sec. 11.3). Dilute the sample as needed using 4.1 g/L sodium hydroxide so that the concentration is within the calibration range. Analyze the diluted sample using a 3.00 mL aliquot as described in Section 11.3. Correct the final concentration result by multiplying by the appropriate dilution factor.

12.3 In the case of an extract, calculate the actual free cyanide concentration in the original solid that was extracted as follows:

$$\frac{\mu g}{g} \text{ free } CN^- \text{ in solid sample} = \frac{\mu g}{L} \text{ free } CN^- \text{ in extract sample} \times \frac{\text{Final extract solution volume (L)}}{\text{Sample mass (g)}}$$

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 criteria for users of the methods. Instead, performance criteria 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 Water Samples – Round-robin test data obtained from the results of four individual operators in four independent laboratories and in a variety of water matrices (Refs. 7 and 7) are presented in Table 1. The bias and overall (between-laboratory) and single-operator precision for water samples, based on the collaborative test data is presented in Table 2. These data are provided for guidance purposes only.

13.3 Solid Samples – Round-robin test data obtained from the results of four individual operators in four laboratories and in a variety of solid matrices (Ref. 7) are presented in Table 3. The bias and overall (between-laboratory) and single-operator

precision for solid samples based on the collaborative test data is presented in Table 4. These data are provided for guidance purposes only.

As with most such evaluations, the test method was intentionally challenged via the analysis of a range of solid materials from the most simple (i.e., sand matrix) to the most complex. Of noteworthy consequence is the fact that the manufactured gas plant sample was obtained from a former on-site landfill, in which an enormous variety of wastes had been historically deposited. In particular, the manufactured gas plant sample was known to contain "purifier-box" wastes, which are relatively acidic (pH ≤ 4) solid wastes that frequently contain free iron at moderate-to-high concentrations. The presence of large quantities of free iron can induce skewed and highly variable results, due to its complexation with free cyanide during the extraction procedure. Additionally, purifier-box wastes contain sulfur species, many of which, are well-known interferences in cyanide analysis. Given its complexity, the disparate results for the manufactured gas plant sample (Table 4) were not unexpected and serve to emphasize the need, under specific circumstances, to modify the extraction procedure in order to obtain improved free cyanide analysis results so as to meet the data quality objectives of the project.

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 operations. 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

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17.0 TABLES, DIAGRAMS, FLOW CHARTS, AND VALIDATION DATA

The following pages contain the tables and figures referenced by this method.

TABLE 1

RESULTS OF INTERLABORATORY TESTING FOR FREE CYANIDE BY MICRODIFFUSION ANALYSIS IN REAL-WORLD WATER SAMPLES

Reagent Water

	Lab 1						Lab 2						Lab 3						Lab 4					
True Value (µg/L Free CN^-)	1	2	3	Avg Recovery (µg/L Free CN^-)	% Recovery	% RSD	1	2	3	Avg Recovery (µg/L Free CN^-)	% Recovery	% RSD	1	2	3	Avg Recovery (µg/L Free CN^-)	% Recovery	% RSD	1	2	3	Avg Recovery (µg/L Free CN^-)	% Recovery	% RSD
5.0	7.4	6.6	6.6	6.9 ± 0.46	137	6.7	5.7	6.2	5.7	5.9 ± 0.29	117	4.9	3.9	4.5	3.7	4.0 ± 0.42	81	10	4.9	5.0	4.9	4.9 ± 0.06	99	1.2
125	151	152	146	150 ± 3.4	120	2.3	129	128	118	125 ± 6	100	4.9	133	116	121	123 ± 9	99	7.1	120	120	120	120 ± 0.06	96	0.048
250	268	266	270	268 ± 2.0	107	0.75	249	230	236	238 ± 10	95	4.1	266	240	249	252 ± 13	101	5.3	247	247	247	247 ± 0.06	99	0.023

Aluminum Reduction Plant Waste Water

	Lab 1						Lab 2						Lab 3						Lab 4					
True Value (µg/L Free CN^-)	1	2	3	Avg Recovery (µg/L Free CN^-)	% Recovery	% RSD	1	2	3	Avg Recovery (µg/L Free CN^-)	% Recovery	% RSD	1	2	3	Avg Recovery (µg/L Free CN^-)	% Recovery	% RSD	1	2	3	Avg Recovery (µg/L Free CN^-)	% Recovery	% RSD
5.0	6.0	6.8	5.6	6.1 ± 0.61	123	10	5.2	5.2	4.7	5.0 ± 0.29	101	5.7	3.9	2.3	4.2	3.5 ± 1.0	69	29	O^a	O^a	O^a	---	---	---
125	144	143	154	147 ± 5.7	118	3.9	117	105	119	114 ± 7.6	91	6.7	131.9	112.5	113.3	119 ± 11	95	9.2	132	132	132	132 ± 0	106	0
250	315	303	297	305 ± 9.1	122	3.0	246	263	257	255 ± 8.6	102	3.4	259.9	225.7	223.1	236 ± 21	94	8.7	O^b	O^b	O^b	---	---	---

MGP Waste Site Ground Water

	Lab 1						Lab 2						Lab 3						Lab 4					
True Value (µg/L Free CN^-)	1	2	3	Avg Recovery (µg/L Free CN^-)	% Recovery	% RSD	1	2	3	Avg Recovery (µg/L Free CN^-)	% Recovery	% RSD	1	2	3	Avg Recovery (µg/L Free CN^-)	% Recovery	% RSD	1	2	3	Avg Recovery (µg/L Free CN^-)	% Recovery	% RSD
5.0	7.4	8.2	7.4	7.7 ± 0.46	153	6.0	3.4	4.4	4.6	4.1 ± 0.64	83	16	4.3	4.3	4.6	4.4 ± 0.17	88	3.9	4.3	4.4	NA	4.4 ± 0.071	87	1.6
125	144	137	147	143 ± 5.2	114	3.7	109	114	127	117 ± 9	93	8.0	117	116	118	117 ± 1.0	94	0.87	116	115	NA	116 ± 0.64	93	0.55
250	276	277	279	277 ± 1.3	111	0.5	262	259	259	260 ± 2	104	0.67	239	245	242	242 ± 2.8	97	1.2	223	222	NA	223 ± 0.64	89	0.29

MGP Waste Site Surface Water

	Lab 1						Lab 2						Lab 3						Lab 4					
True Value (µg/L Free CN^-)	1	2	3	Avg Recovery (µg/L Free CN^-)	% Recovery	% RSD	1	2	3	Avg Recovery (µg/L Free CN^-)	% Recovery	% RSD	1	2	3	Avg Recovery (µg/L Free CN^-)	% Recovery	% RSD	1	2	3	Avg Recovery (µg/L Free CN^-)	% Recovery	% RSD
5.0	5.8	5.4	5.0	5.4 ± 0.40	108	7.4	5.4	5.1	5.1	5.2 ± 0.17	104	3.3	3.7	4.2	3.7	3.9 ± 0.29	77	7.5	4.0	4.0	NA	4.0 ± 0	80	0
125	116	120	115	117 ± 2.4	93	2.1	128	131	124	128 ± 3.5	102	2.8	115	116	116	116 ± 0.50	93	0.43	117	117	NA	117 ± 0	94	0
250	313	321	301	312 ± 10	125	3.2	262	245	253	253 ± 8.5	101	3.4	247	243	245	245 ± 2.0	98	0.81	245	245	NA	245 ± 0	98	0

Drinking Water

	Lab 1						Lab 2						Lab 3						Lab 4					
True Value (µg/L Free CN^-)	1	2	3	Avg Recovery (µg/L Free CN^-)	% Recovery	% RSD	1	2	3	Avg Recovery (µg/L Free CN^-)	% Recovery	% RSD	1	2	3	Avg Recovery (µg/L Free CN^-)	% Recovery	% RSD	1	2	3	Avg Recovery (µg/L Free CN^-)	% Recovery	% RSD
5.0	8.2	8.2	7.8	8.1 ± 0.23	161	2.9	4.9	5.2	5.2	5.1 ± 0.17	102	3.4	4.7	4.7	4.4	4.6 ± 0.17	92	3.8	4.6	4.6	NA	4.6 ± 0	92	0
125	141	148	148	145 ± 3.7	116	2.5	113	132	134	126 ± 12	101	9.2	128	120	116	121 ± 6.4	97	5.3	116	115	NA	116 ± 0.71	92	0.61
250	235	247	233	238 ± 7.6	95	3.2	276	226	265	256 ± 26	102	10	254	247	244	249 ± 5.1	99	2.1	249	248	NA	249 ± 0.71	99	0.28

NA = Not analyzed
O^a = Outlier data that were detected and removed during the current study
O^b = Outlier data that were removed during the previous study (see Reference 6)

Data were obtained from Reference 7.

TABLE 2

PRECISION AND BIAS OF MICRODIFFUSION FREE CYANIDE METHOD
IN WATER SAMPLES

Matrix	No. of Labs	Free CN^- True Value (µg/L)	Grand Mean (µg/L)	Relative Bias	Repeatability (RSD)[a]	Reproducibility (RSD)[b]
Reagent Water	**4**	5.0	5.43	8.5%	6.7%	21.9%
	4	125	130	3.6%	4.1%	11.4%
	4	250	251	0.5%	3.1%	5.6%

Matrix	No. of Labs	Free CN^- True Value (µg/L)	Grand Mean (µg/L)	Relative Bias	Repeatability (RSD_r)	Reproducibility (RSD_R)
Aluminum Reduction Plant Waste Water	**3**	5.0	4.88	-2.4%	17%	35%
	4	125	128	2.4%	5.6%	13%
	3	250	266	6.2%	3.8%	14%

Matrix	No. of Labs	Free CN^- True Value (µg/L)	Grand Mean (µg/L)	Relative Bias	Repeatability (RSD_r)	Reproducibility (RSD_R)
MGP Waste Site Ground Water	**4**	5.0	5.14	2.7%	7.9%	37%
	4	125	123	-1.6%	4.0%	11%
	4	250	250	0.19%	0.71%	8.1%

Matrix	No. of Labs	Free CN^- True Value (µg/L)	Grand Mean (µg/L)	Relative Bias	Repeatability (RSD_r)	Reproducibility (RSD_R)
MGP Waste Site Surface Water	**4**	5.0	4.62	-7.7%	5.5%	17%
	4	125	119	-4.5%	2.1%	5.5%
	4	250	264	5.5%	3.0%	14%

Matrix	No. of Labs	Free CN^- True Value (µg/L)	Grand Mean (µg/L)	Relative Bias	Repeatability (RSD_r)	Reproducibility (RSD_R)
Drinking Water	**4**	5.0	5.59	12%	2.6%	33%
	4	125	127	1.7%	3.8%	11%
	4	250	248	-0.90%	7.0%	5.2%

[a]Single-laboratory precision
[b]Overall (between-laboratory) precision

Based on data obtained from Reference 7.

TABLE 3

RESULTS OF INTERLABORATORY TESTING FOR FREE CYANIDE BY MICRODIFFUSION ANALYSIS IN REAL-WORLD SOLID SAMPLES

Extract of a Natural Sand[a]

	Lab 1					Lab 2					Lab 3					Lab 4				
True Value (µg/L Free CN^-)	1	2	Avg Recovery (µg/L Free CN^-)	% Recovery	% RSD	1	2	Avg Recovery (µg/L Free CN^-)	% Recovery	% RSD	1	2	Avg Recovery (µg/L Free CN^-)	% Recovery	% RSD	1	2	Avg Recovery (µg/L Free CN^-)	% Recovery	% RSD
118	111	116	113 ± 3.394	96	3.0	123	116	120 ± 4.9	101	4.1	123	119	121 ± 2.8	102	2.3	128	126	127 ± 1.4	107	1.1

Ottawa Sand[b]

	Lab 1					Lab 2					Lab 3					Lab 4				
True Value (µg/g Free CN^-)	1	2	Avg Recovery (µg/g Free CN^-)	% Recovery	% RSD	1	2	Avg Recovery (µg/g Free CN^-)	% Recovery	% RSD	1	2	Avg Recovery (µg/g Free CN^-)	% Recovery	% RSD	1	2	Avg Recovery (µg/g Free CN^-)	% Recovery	% RSD
11.6	11.3	10.9	11.1 ± 0.283	96	2.5	11.3	11.0	11.2 ± 0.2	96	1.9	9.80	9.80	9.80 ± 0	84	0	9.90	10.2	10.1 ± 0.2	87	2.1

Aluminum Reduction Plant Soil[b]

	Lab 1					Lab 2					Lab 3					Lab 4				
True Value (µg/g Free CN^-)	1	2	Avg Recovery (µg/g Free CN^-)	% Recovery	% RSD	1	2	Avg Recovery (µg/g Free CN^-)	% Recovery	% RSD	1	2	Avg Recovery (µg/g Free CN^-)	% Recovery	% RSD	1	2	Avg Recovery (µg/g Free CN^-)	% Recovery	% RSD
43.5	43.0	39.7	41.3 ± 2.369	95	5.7	40.8	42.4	41.6 ± 1.2	96	2.8	38.2	37.0	37.6 ± 0.8	86	2.2	37.9	39.4	38.7 ± 1.1	89	2.7

Mixed Manufactured Gas Plant Waste[b,c]

	Lab 1					Lab 2					Lab 3					Lab 4				
True Value (µg/g Free CN^-)	1	2	Avg Recovery (µg/g Free CN^-)	% Recovery	% RSD	1	2	Avg Recovery (µg/g Free CN^-)	% Recovery	% RSD	1	2	Avg Recovery (µg/g Free CN^-)	% Recovery	% RSD	1	2	Avg Recovery (µg/g Free CN^-)	% Recovery	% RSD
32.8	40.4	38.5	39.4 ± 1.308	120	3.3	18.6	18.9	18.7 ± 0.2	57	1.1	14.0	13.4	13.7 ± 0.4	42	3.1	9.20	8.90	9.05 ± 0.2	28	2.3

[a]One extract was prepared from a natural sand sample, following the procedural guidance for solid samples given in the method. This single extract was analyzed by four different analysts, each located at four independent laboratories.
[b]Sample extraction and analysis were carried out individually at each of the four participating independent laboratories.
[c]A complex, mixed-waste sample comprised of purifier-box waste, and a variety of other solid and hazardous waste materials.

Data were obtained from Reference 7.

TABLE 4

PRECISION AND BIAS OF MICRODIFFUSION FREE CYANIDE METHOD
IN REAL-WORLD SOLID SAMPLES

Matrix	No. of Labs	Free CN^- True Value	Grand Mean (µg/L)	Relative Bias	Repeatability (RSD_r)[a]	Reproducibility (RSD_R)[b]
Natural Sand Extract[c]	**4**	118	120	1.7%	2.8%	5.1%

Matrix	No. of Labs	Free CN^- True Value (µg/g)	Grand Mean (µg/g)	Relative Bias	Repeatability (RSD_r)	Reproducibility (RSD_R)
Ottawa Sand[d]	**4**	11.6	10.5	-9.3%	2.0%	6.8%

Matrix	No. of Labs	Free CN^- True Value (µg/g)	Grand Mean (µg/g)	Relative Bias	Repeatability (RSD_r)	Reproducibility (RSD_R)
Aluminum Reduction Plant Soil[d]	**4**	43.5	39.8	-8.5%	3.7%	5.6%

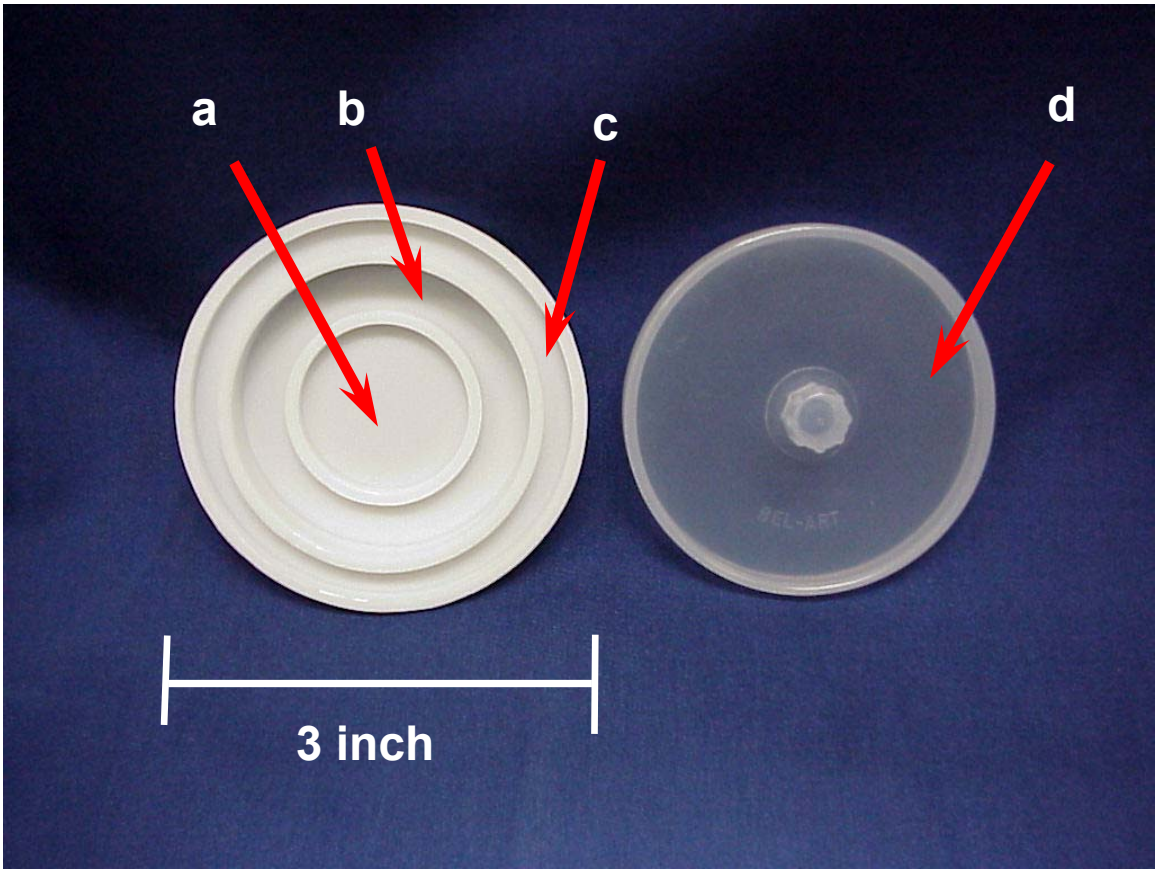
Matrix	No. of Labs	Free CN^- True Value (µg/g)	Grand Mean (µg/g)	Relative Bias	Repeatability (RSD_r)	Reproducibility (RSD_R)
Mixed Manufactured Gas Plant Waste[d,e]	**4**	32.8	20.2	-38%	3.5%	66%

[a]Single-laboratory precision
[b]Overall (between-laboratory) precision
[c]One extract was prepared from a natural sand sample, following the procedural guidance for solid samples given in the method. This single extract was analyzed by four different analysts, each located at four independent laboratories.
[d]Sample extraction and analysis were carried out individually at each of the four participating independent laboratories.
[e]A complex, mixed-waste sample comprised of purifier-box waste, and a variety of other solid and hazardous waste materials.

Based on data obtained from Reference 7.

FIGURE 1

MICRODIFFUSION CELL



a) Center cell chamber for containment of sodium hydroxide absorber solution;
b) Outer cell chamber for introduction of sample;
c) Groove for holding and sealing cell cover; and
d) Cell cover

FIGURE 2

MICRODIFFUSION PROCESS OVERVIEW

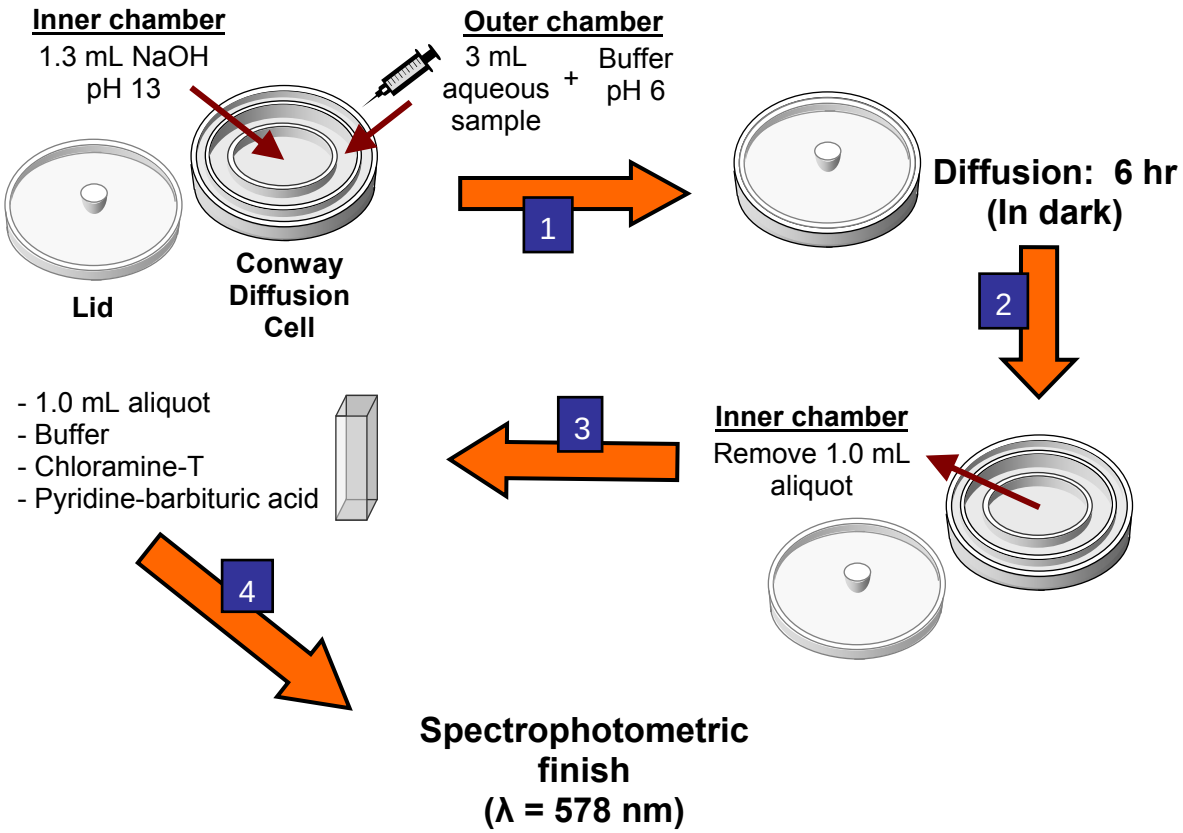
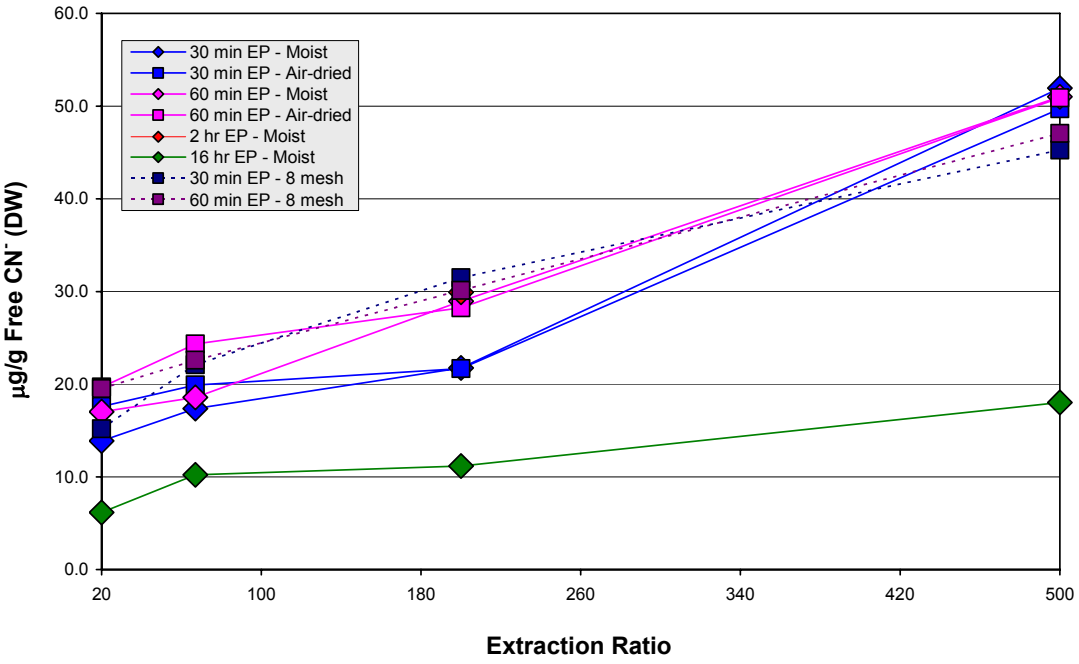


FIGURE 3

EXTRACTION OF FREE CN^- AS A FUNCTION OF EXTRACTION RATIO FOR VARIOUS EXTRACTION PERIODS (EP) IN A MANUFACTURED GAS PLANT SOIL



Data were obtained from Reference 7.

FIGURE 4

DISTRIBUTION OF HCN AND CN^- SPECIES CONCENTRATIONS IN AQUEOUS SOLUTION AS A FUNCTION OF pH AT 25 °C

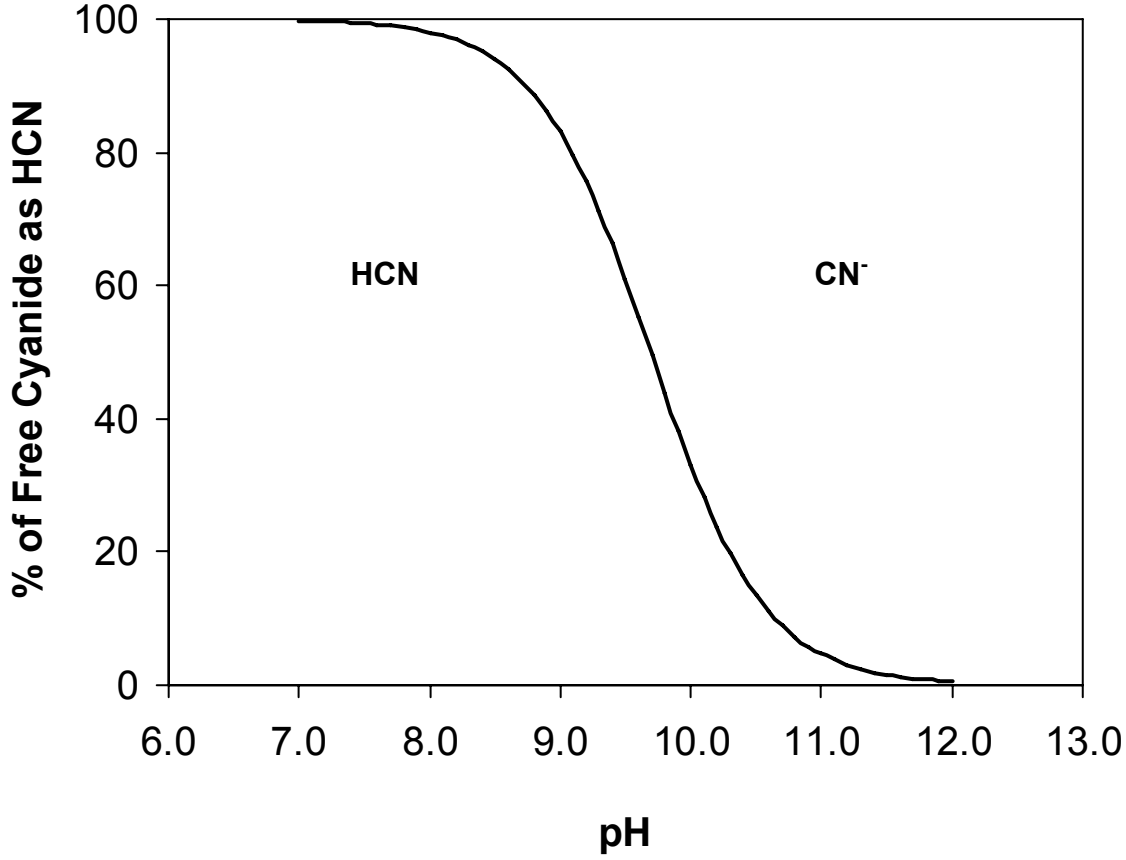
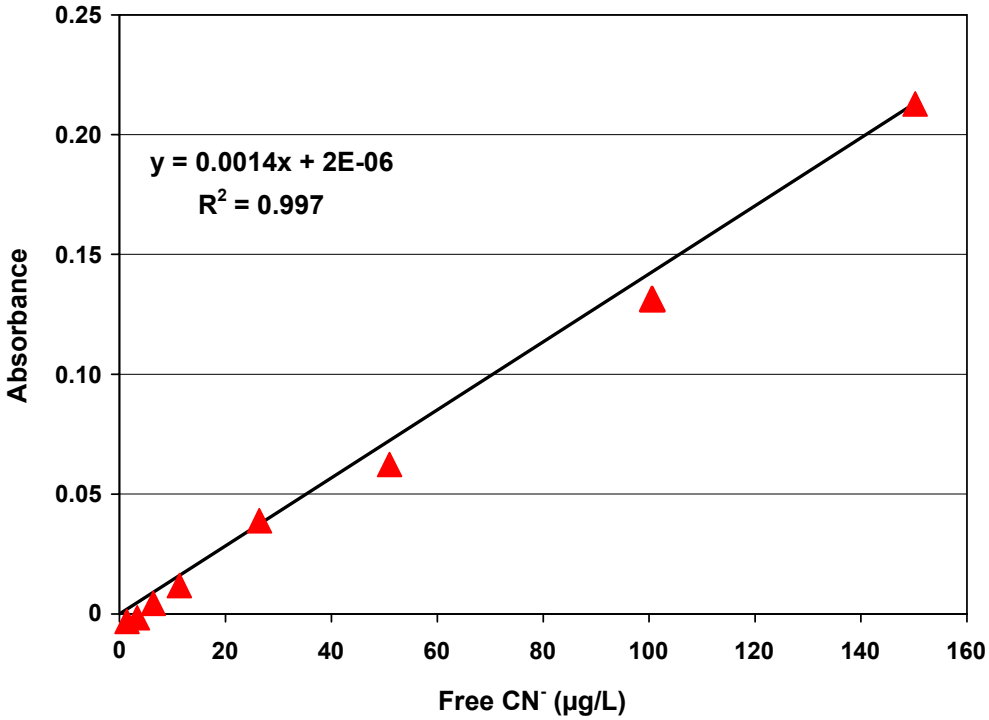


Figure obtained from Reference 4.

FIGURE 5

EXAMPLE FREE CYANIDE CALIBRATION CURVE



Data taken from Reference 6.