METHOD 9013A

CYANIDE EXTRACTION PROCEDURE FOR SOLIDS AND OILS

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

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

1.0 SCOPE AND APPLICATION

1.1 The extraction procedure described in this method is designed for the extraction of soluble and insoluble cyanides from solid, oil, and multi-phase wastes. The resulting extraction solutions may be analyzed for total cyanide and/or cyanides amenable to chlorination (e.g., Methods 9010, 9012 and 9014) as well as analyzed for metal cyanide complexes (e.g., Method 9015).

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

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

1.3 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

The waste sample is extracted with water at pH 10 or greater, and the extract distilled and analyzed (e.g., by Methods 9010, 9012 and 9014). Samples that contain free water are filtered and separated into an aqueous component and a combined oil and solid component. The nonaqueous component is then extracted, and an aliquot of the extract combined with an aliquot of the filtrate in proportion to the composition of the sample. Alternatively, the components may be analyzed separately, and cyanide levels reported for each component. .

In the presence of free iron and high levels of suspended solids, some cyanide may combine with iron to form iron cyanide precipitates or possibly adsorb to suspended solids under the very low pH conditions encountered during the total cyanide distillation step (e.g., Methods 9010 and 9012) (Refs. 1-6). When this occurs, some cyanide may remain in the distillation flask and not be distilled over into the absorber solution, resulting in incomplete recovery of cyanide. Therefore, alkaline extraction followed by distillation and analysis of the extract is the preferred method for determining total and amenable cyanide in solid samples.

NOTE: This method has not been validated for recovery of free cyanide. Studies indicate that free cyanide may not be fully recovered for certain waste types. If recovery of free cyanide is important to meet project objectives, spiking studies should be performed for the specific matrices being tested.

3.0 DEFINITIONS

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

4.0 INTERFERENCES

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

4.2 Chlorine and sulfide are potential interferences in this method. Interferences are eliminated or reduced by using the distillation procedure. Distillation of samples for cyanide can result in both positive and negative bias depending upon the matrix of the sample. All interferences should be evaluated prior to the distillation of unknown samples. Negative bias is detected by incomplete spike recoveries. Positive bias cannot be detected using matrix spikes. Thiosulfate, sulfite, and other Sulfur (IV) oxides react with cyanide during distillation resulting in a negative bias. Levels of the compounds below 20 mg/L do not generally interfere.

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

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

NOTE: ASTM studies have indicated that $[Fe(CN)_6]^{-3}$ recoveries may be low when distilling samples containing bismuth nitrate.

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

4.6 Thiocyanate is reported to be an interferent when present at very high levels. Levels greater than 10 mg/L can interfere by decreasing the cyanide concentration. Nitrate and thiocyanate combined is a positive interference.

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

5.0 SAFETY

5.1 This method does not address all safety issues associated with its use. The laboratory is responsible for maintaining a safe work environment and a current awareness file of OSHA regulations regarding the safe handling of the chemicals specified in this method. A reference file of material safety data sheets (MSDSs) should be available to all personnel involved in these analyses.

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

5.2 Because of the toxicity of cyanide, exercise great care in its handling. Acidification of cyanide solutions produces toxic, gaseous hydrogen cyanide (HCN). Perform all manipulations in the hood so that any HCN gas that is formed is safely vented. Wear hand and eye protection at all times when working with cyanide.

6.0 EQUIPMENT AND SUPPLIES

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

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

6.1 Extractor - Any suitable device that sufficiently agitates a sealed container of one liter volume or greater. For the purpose of this analysis, agitation is sufficient when (1) all sample surfaces are continuously brought into contact with extraction fluid, and (2) the agitation prevents stratification of the sample and fluid.

6.2 Buchner funnel apparatus

6.2.1 Buchner funnel - 500-mL capacity, with 1-L vacuum filtration flask

6.2.2 Glass wool - Suitable for filtering, 0.8-µm diameter such as Corning Pyrex 3950

6.2.3 Millipore 0.45-µm membrane filters - Suitable for filtering into a vacuum filtration flask

6.2.4 Vacuum source - Vacuum pump or a water driven aspirator. A valve or stopcock to release vacuum is required.

6.3 Top-loading balance - Capable of weighing 0.1 g

6.4 Separatory funnels - 500-mL

6.5 pH papers or test strips

7.0 REAGENTS AND STANDARDS

7.1 Reagent grade chemicals must be used in all tests. Unless otherwise indicated, it is intended that all reagents conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available. Other grades may be used, provided it is first ascertained that the reagent is of sufficiently high purity to permit its use without lessening the accuracy of the determination. Reagents should be stored in glass to prevent the leaching of contaminants from plastic containers. Note, however, that sodium hydroxide solutions of relatively moderate strength (i.e., 4.1 g/L and greater), should be stored in HDPE plastic containers whenever possible.

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

7.3 Sodium hydroxide (50% w/v), NaOH - Commercially available

7.4 Sulfuric acid (50%v/v), H_2SO_4 - Commercially available

7.5 n-Hexane, C_6H_{14}

8.0 SAMPLE COLLECTION, PRESERVATION, AND STORAGE

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

8.1 See the introductory material to Chapter Three, “Inorganic Analytes.”

8.2 Samples should be collected in plastic or glass (preferably plastic) containers that are either amber or covered with aluminum foil so as to filter light at 400 nm and below and prevent photodecomposition of 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 Store solid samples at ≤6 ºC after collection and prior to extraction. Bring samples to room temperature just prior to extraction.

8.4 Store solid samples at ≤6 ºC for no longer than 14 days. Solid phase samples must be extracted within 14 days of sample collection.

8.5 After generation, store solid phase extract solutions at ≤6 ºC prior to analysis by the determinative method. Bring the extract solutions to room temperature just prior to analysis.

8.6 Store solid phase extract solutions at ≤6 ºC for no longer than 14 days. Analysis of solid phase extracts must be performed within 14 days of extract generation.

8.7 If fatty acids, detergents, and surfactants are a problem, they may be extracted using the following procedure. Acidify the sample with acetic acid (1.6 M) to pH 6.0 to 7.0.

CAUTION: This procedure can produce lethal HCN gas.

Extract with isooctane, hexane, or chloroform (preference in order named) with solvent volume equal to 20% of the sample volume. One extraction is usually adequate to reduce the compounds below the interference level. Avoid multiple extractions or a long contact time at low pH in order to keep the loss of HCN at a minimum. When the extraction is completed, immediately raise the pH of the sample to 12 with a 50% NaOH solution.

8.7 Also see the applicable distillation and determinative method for additional guidance.

9.0 QUALITY CONTROL

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

9.2 Initial demonstration of proficiency

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 target analytes 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.

9.3 Initially, 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 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.

9.4.1 Method blank - For each batch of solid phase samples extracted using this method, at least one method blank should also be carried through the entire sample extraction, preparation and analytical process. A method blank is prepared by using a specified volume or weight of the extraction solution and then carrying it through the appropriate steps of the extraction and analytical process. These steps may include, but are not limited to, prefiltering, extraction, dilution, filtering, and analysis. If the method blank does not contain target analytes at a level that exceeds the project specific criteria requirements, then the method blank would be considered acceptable. In the absence of project specific criteria, if the blank is less than the lower limit of detection, less than 10% of the regulatory limit, or less than 10% of the lowest sample concentration, whichever is greater, then the method blank is considered acceptable. If the method blank cannot be considered acceptable, the method blank should be re-run once, and if still unacceptable, then all samples after the last acceptable method blank must be prepared again and reanalyzed along with the other appropriate batch QC samples. These blanks will be useful in determining if samples are being contaminated. If the method blank exceeds the criteria, but the samples are all either below the reporting level or below the applicable action level or other criteria, then the data should not be rejected based on this analysis.

9.4.2 Matrix spike (MS)/ Duplicate - For each batch of solid phase samples extracted using this method, at least one matrix spike (MS) and one duplicate unspiked

sample or one matrix spike/matrix spike duplicate (MS/MSD) pair should be carried through the entire sample extraction, preparation and analytical process. Spiking is performed directly on the solid sample matrix prior to extraction in order to assess the efficiency of the extraction procedure. 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. A separate spiked sample and a separate duplicate unspiked sample may be analyzed in lieu of MS/MSD analyses.

9.4.3 LCS - For each batch of samples processed, at least one LCS must be carried through the entire sample preparation and analytical process, as described in Chapter One. The LCS is a reagent water solution fortified with method analytes at known concentrations, prepared from a different source than that used to prepare the calibration standards. The LCS should be spiked with each analyte of interest at the project-specific action level or when lacking project specific action levels, between the low- and mid-level standards. Concurrent analyses of standard reference materials (SRMs) containing known values of analytes in the media of interest are recommended and may be used as an LCS.

NOTE: If insoluble or complexed cyanides (such as Prussian blue) are of interest, the recovery of cyanide should be evaluated from a similar species as that which is expected to be present in the samples.

9.4.4 In order to verify the extraction process at the Lower Level of Quantitation (LLOQ), 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 within established limits, or other such project required acceptance limits, for precision and bias to verify the data reporting limits. Until the laboratory has sufficient data to determine acceptance limits statistically, a limit of 20% +/- the LCS Criteria may be used for the LLOQ acceptance criteria. The frequency of this LLOQ verification is not mandated, but should be determined by the laboratory's quality plan. Additional information on LLOQ can be found in 8000D, Section 9.7.

9.5 Standard quality assurance practices should be used with this method as included in appropriate systematic planning documents and laboratory SOPs.

9.6 Also refer to the applicable distillation and determinative method for appropriate quality control guidelines.

10.0 CALIBRATION AND STANDARDIZATION

There are no calibration or standardization steps directly associated with this procedure.

11.0 PROCEDURE

11.1 If the waste does not contain any free aqueous phase, go to Sec. 11.6. If the sample is a homogeneous fluid or slurry that does not separate or settle in the distillation flask when using a polytetrafluorethylene (PTFE) coated magnetic stirring bar (but mixes so that the solids are entirely suspended); the sample may be analyzed by Method 9010 without an extraction step.

11.2 Assemble Buchner funnel apparatus. Unroll glass filtering fiber and fold the fiber over itself several times to make a pad about 1 cm thick when lightly compressed. Cut the pad to fit the Buchner funnel. Weigh the pad, and then place it in the funnel. Turn the aspirator on and wet the pad with a known amount of water.

11.3 Transfer the sample to the Buchner funnel in small aliquots, first decanting the fluid. Rinse the sample container with known amounts of water and add the rinses to the Buchner funnel. Record the total volume of rinses used. When no free water remains in the funnel, slowly open the stopcock to allow air to enter the vacuum flask. A small amount of sediment may have passed through the glass fiber pad. This will not interfere with the analysis.

11.4 Transfer the solid and the glass fiber pad to a tared weighing dish. Since most greases and oils will not pass through the fiber pad, solids, oils, and greases will be extracted together. If the filtrate includes an oil phase, transfer the filtrate to a separatory funnel. Collect and measure the volume of the aqueous phase. Transfer the oil phase to the weighing dish with the solid.

11.5 Weigh the dish containing solid, oil (if any), and filter pad. Subtract the weight of the dry filter pad. Calculate the net volume of water present in the original sample by subtracting the total volume of rinses used from the measured volume of the filtrate.

11.6 Place the following in a 1-L, wide-mouthed bottle:

500 mL water,
5 mL 50% w/v NaOH, and
50 mL n-hexane (if a heavy grease is present).

If the weight of the solids (Sec. 11.5) is greater than 25 g, weigh out a representative aliquot of 25 g and add it to the bottle; otherwise add all of the solids. Cap the bottle.

11.7 The extract must be maintained above pH 10 throughout the extraction step and subsequent filtration. Since some samples may release acid, the pH must be monitored as follows. Shake the extraction bottle and after one minute, check the pH. If the pH is below 12, add 50% NaOH in 5 mL increments until it is at least 12. Recap the bottle, and repeat the procedure until the pH does not drop.

11.8 Place the bottle or bottles in the tumbler, making sure there is enough foam insulation to cushion the bottle. Turn the tumbler on and allow the extraction to run for about 16 hours.

11.9 For extract solutions to be subsequently distilled for total cyanide or cyanides amenable to chlorination (e.g., Method 9010 or 9012):

11.9.1 Prepare a Buchner funnel apparatus as in Sec. 11.2 with a glass fiber pad filter.

11.9.2 Decant the extract to the Buchner funnel. Full recovery of the extract is not necessary.

11.10 For extract solutions to be subsequently analyzed for metal cyanide complexes (Method 9015):

11.10.1 Check the pH of the extraction solution. Adjust the pH to between 11 and 12, using 50% H_2SO_4. Recap the bottle and mix the solution. Repeat the procedure until the pH is in the proper range.

11.10.2 Prepare a Buchner funnel apparatus with a 0.45-µm membrane filter.

11.10.3 Decant the extract to the Buchner funnel. Full recovery of the extract is not necessary.

11.11 If the extract contains an oil phase, separate the aqueous phase using a separatory funnel. Neither the separation nor the filtration are critical, but are necessary to be able to measure the volume of the aliquot of the aqueous extract analyzed. Small amounts of suspended solids and oil emulsions will not interfere.

11.12 At this point, an aliquot of the filtrate of the original sample may be combined with an aliquot of the extract in a proportion representative of the sample. Alternatively, they may be distilled and analyzed separately and concentrations given for each phase. This is described by the following equation:

$$\frac{\text{Liquid Sample Aliquot (mL)}}{\text{Extract Aliquot (mL)}} = \frac{\text{Solid Extracted (g)}^{a}}{\text{Total Solid (g)}^{b}} \times \frac{\text{Total Sample Filtrate (mL)}^{c}}{\text{Total Extraction Fluid (mL)}^{d}}$$

[a] From Sec. 11.6. Weight of solid sample used for extraction.

[b] From Sec. 11.5. Weight of solids and oil phase with the dry weight of filter and tared dish subtracted.

[c] Includes volume of all rinses added to the filtrate (Secs. 11.2 and 11.3).

[d] 500 mL of water plus total volume of NaOH solution. Does not include hexane, which is subsequently removed (Sec. 11.11).

Alternatively, the aliquots may be distilled and analyzed separately, concentrations for each phase reported separately, and the amounts of each phase present in the sample reported separately.

11.13 Determination of percent dry weight

In certain cases, the reporting of sample results is desired based on a dry weight basis. When such data are desired, a separate portion of sample for this determination should be weighed out at the same time as the portion used for analytical determination.

CAUTION: The drying oven should be contained in a hood or vented. Significant laboratory contamination may result from a heavily contaminated waste material.

11.13.1 Immediately after weighing the sample aliquot to be extracted, weigh an additional 5-10 g aliquot of the sample into a tared crucible. Dry this aliquot overnight at 105 °C. Allow to cool in a desiccator before weighing.

11.13.2. Calculate the % dry weight as follows:

$$\% \text{ Dry Weight} = \frac{\text{g of dry sample}}{\text{g of sample}} \times 100$$

NOTE: This oven-dried aliquot is not used for the extraction and should be appropriately disposed of once the dry weight is determined.

12.0 DATA ANALYSIS AND CALCULATIONS

12.1 There are no determinative data analysis and calculation steps directly associated with this procedure. Follow the directions given in the determinative method.

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

13.0 METHOD PERFORMANCE

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

13.2 In a single laboratory study, recoveries of 78-95% were reported for soils spiked with $Fe_4[Fe(CN)_6]_3$, an insoluble iron cyanide compound (see Table 1.). These data are provided for guidance purposes only.

14.0 POLLUTION PREVENTION

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

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

15.0 WASTE MANAGEMENT

The Environmental Protection Agency requires that laboratory waste management practices be conducted consistent with all applicable rules and regulations. The Agency urges laboratories to protect the air, water, and land by minimizing and controlling all releases from hoods and bench operations, complying with the letter and spirit of any sewer discharge permits and regulations, and by complying with all solid and hazardous waste regulations, particularly the hazardous waste identification rules and land disposal restrictions. For further information on waste management, consult the ACS publication listed in Sec. 14.2.

16.0 REFERENCES

1. American Society for Testing and Materials, "Understanding Cyanide Species," D 6696, ASTM International, 2004. This reference can be purchased on line at ASTM's web site: www.astm.org.

2. R. S. Ghosh, D. A. Dzombak, R. G. Luthy, "Equilibrium Precipitation and Dissolution of Iron Cyanide Solids in Water," *Environ. Eng. Sci.*, Vol. 16, 293-313, 1999.

3. J. C. L. Meeussen, M. G. Keizer, W. H. van Riemsdijk, F. A. M. de Haan, "Dissolution Behavior of Iron Cyanide (Prussian Blue) in Contaminated Soils," *Environ. Sci. Technol.*, Vol. 26, 1832-1838, 1992.

4. J. C. L Meeussen, W. H. Keizer, F. A. M. de Haan, "Chemical Stability and Decomposition Rate of Iron Cyanide Complexes in Soil Solutions," *Environ. Sci. Technol.*, Vol. 26, 511-516, 1992.

5. J. T. Bushey, D. A. Dzombak, "Ferrocyanide Adsorption on Aluminum Oxides," *J. Coll. Int. Sci.*, Vol. 272, 46-51, 2004.

6. T. L. Theis, M. L West, "Effects of Cyanide Complexation on the Adsorption of Trace Metals at the Surface of Goethite," *Environ. Technol. Letters*, Vol. 7, 309-318, 1986.

7. The RETEC Group, Inc., "Metal Cyanide Complexes by Anion Exchange Chromatography and UV Detection Method Validation Summary Report," March, 2004.

17.0 TABLES, DIAGRAMS, FLOWCHARTS, AND VALIDATION DATA

The following page contains the table referenced by this method.

TABLE 1

EXAMPLE TOTAL CYANIDE RECOVERIES IN SPIKED SOILS PREPARED USING METHOD 9013 EXTRACTION

Sample	Background Total Cyanide Concentration[a] (µg/g Cyanide)	Spiking Concentration[b] (µg/g Cyanide)	Average Total Cyanide Recovery[b]	Standard Deviation[c]
Soil 1	0.44	500	95%	1.8% (n = 2)
Soil 2	0.17	500	78%	0.1% (n = 2)
Soil 3	ND	500	86%	6.4% (n = 4)

[a]Total cyanide was determined in the soil extraction solutions using Methods 9010 and 9012.

[b]Soils were spiked using solid $Fe_4[Fe(CN)_6]_3$ prior to extraction.

[c]n = Number of replicate analyses

These data are provided for guidance purposes only.

Data taken from Reference 7.

Appendix A
Summary of Revisions to Method 9013 (From Revision 1, November 2004)

1. Improved overall method formatting for consistency with new SW-846 methods style guidance. The version number was changed to two and the date published was updated to July 2014.
2. Significantly updated and expanded "QUALITY CONTROL" section (Sec. 9.0) for better adherence to current SW-846 method guidelines and for improved alignment with current universal practices for published analytical methods.
3. Updated "INTERFERENCES" in section 4 to add additional information on the effects of certain interferences and deleted reference to method 9010.
4. The method performance information was updated in Section 13.2 and Table 1.
5. Minor editorial and technical revisions were made throughout to improve method clarity.
6. Inserted new section (Sec. 9.4.4) describing the preparation and use of an LLOQ standard.