

METHOD 9013A

CYANIDE EXTRACTION PROCEDURE FOR SOLIDS AND OILS

SW-846 is not an analytical training manual. Therefore, method directions assume that they will be followed by individuals 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.

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 solids and oil wastes. The resulting extraction solutions may be analyzed for total cyanide and/or cyanides amenable to chlorination (Methods 9010, 9012 and 9014) (Refs. 1-3) as well as analyzed for metal cyanide complexes (Method 9015) (Ref. 4). The method is applicable to oil, solid, and multiphasic matrices.

1.2 Analysts should consult the disclaimer statement at the front of the manual and the information in Chapter Two, Sec. 2.1, 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 Use of this method is restricted to use by, or under supervision of experienced and properly trained laboratory analysts. Each analyst must demonstrate the ability to generate acceptable results with this method.

2.0 SUMMARY OF METHOD

If the waste sample contains so much solid, or solids of such a size as to interfere with agitation and homogenization of the sample mixture in the distillation flask, or so much oil or grease as to interfere with the formation of a homogeneous emulsion, the sample may be 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 may then be 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. However, if the sample solids are known to contain sufficient levels of cyanide (about 50 : g/g) as to be well above the limit of

detection, the extraction step may be deleted and the solids distilled directly by the procedure found in Methods 9010 and 9012. This can be accomplished by diluting a small aliquot of the waste solid (1-10 g) in 500 mL of water in the distillation flask and suspending the slurry during distillation with a magnetic stir-bar.

NOTE: 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 (Methods 9010 and 9012) (Refs. 5-10). 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, extraction followed by distillation and analysis of the extract is the preferred method for determining total and amenable cyanide in solid samples.

3.0 DEFINITIONS

Refer to Chapter One 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 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 Potential interferences that may be encountered during analysis are discussed in the applicable determinative method.

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.

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

6.0 EQUIPMENT AND SUPPLIES

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

This section does not list common laboratory glassware (e.g., beakers and flasks).

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- μ m diameter such as Corning Pyrex 3950.

6.2.3 Millipore 0.45- μ m 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.

7.2 Reagent water. 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), H₂SO₄ . Commercially available.

7.5 n-Hexane, C₆H₁₄.

8.0 SAMPLE COLLECTION, PRESERVATION, AND STORAGE

8.1 See the introductory material to Chapter Three.

8.2 Samples must be collected in polyethylene containers covered in aluminum foil or otherwise equivalent containers such as those composed of amber plastic so as to filter UV light at ≤ 300 nm in order to prevent photodecomposition of metal cyanide complexes.

8.3 Store solid samples at 4 °C after collection and prior to extraction. Bring samples to room temperature just prior to extraction.

8.4 Store solid samples at 4 °C 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 4 °C 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 4 °C for no longer than 14 days. Analysis of solid phase extracts must be performed within 14 days of extract generation.

8.7 Also see the applicable 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 Also refer to Method 9010.

10.0 CALIBRATION AND STANDARDIZATION

There are no calibration or standardization steps directly associated with this procedure. See the determinative method.

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, then 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, 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-liter wide-mouthed bottle:

500 mL water
5 mL 50% w/v NaOH
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 pH of the extract must be maintained above 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 (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% H₂SO₄. 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:

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

^aFrom Sec. 11.6. Weight of solid sample used for extraction.

^bFrom Sec. 11.5. Weight of solids and oil phase with the dry weight of filter and tared dish subtracted.

^cIncludes volume of all rinses added to the filtrate (Secs. 11.2 and 11.3).

^d500 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.

13.2 In a single-laboratory study, recoveries of 60-90% were reported for solids and recoveries of 88-92% were reported for oils.

13.3 In a single laboratory study, recoveries of 78-95% were reported for soils spiked with $\text{Fe}_4[\text{Fe}(\text{CN})_6]_3$, an insoluble iron cyanide compound (See Table 1.).

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* available from the American Chemical Society's Department of Government Relations and Science Policy, 1155 16th St., N.W. Washington, D.C. 20036, <http://www.acs.org>.

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 Waste Management Manual for Laboratory Personnel* available from the American Chemical Society at the address listed in Sec. 14.2.

16.0 REFERENCES

1. U.S. Environmental Protection Agency, "Total and Amenable Cyanide: Distillation," Method 9010, U.S. EPA Office of Solid Waste SW-846 Manual.
2. U.S. Environmental Protection Agency, "Total and Amenable Cyanide (Automated Colorimetric, with Off-Line Distillation)," Method 9012, U.S. EPA Office of Solid Waste SW-846 Manual.
3. U.S. Environmental Protection Agency, "Titrimetric and Manual Spectrophotometric Determinative Methods for Cyanide," Method 9014, U.S. EPA Office of Solid Waste SW-846 Manual.
4. U.S. Environmental Protection Agency, "Metal Cyanide Complexes by Anion Exchange Chromatography and UV Detection," Method 9015, U.S. EPA Office of Solid Waste SW-846 Manual.
5. 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.
6. 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.

7. 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.
8. 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.
9. J. T. Bushey, D. A. Dzombak, "Ferrocyanide Adsorption on Aluminum Oxides," *J. Coll. Int. Sci.*, Vol. 272, 46-51, 2004.
10. 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.
11. 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)

^aTotal cyanide was determined in the soil extraction solutions using EPA SW-846 Method 9010 and 9012.

^bSoils were spiked using solid $\text{Fe}_4[\text{Fe}(\text{CN})_6]_3$ prior to extraction.

^cn = Number of replicate analyses

Data taken from Reference 11.