

Cyanide, Total or Weak Acid Dissociable, by Manual Distillation - PBM

Parameter	Cyanide – Total OR Cyanide - WAD		
Analytical Method	Total Cyanide: Strong acid distillation (H ₂ SO ₄ or HCl – Hydroxylamine Hydrochloride). Weak Acid Dissociable (WAD) Cyanide: Distillation at pH 4.5 – 6.0.		
Introduction	Cyanide-containing compounds occur throughout the environment and may be attributed to both natural and anthropogenic sources. Cyanide may be present in a variety of combinations with alkali metals alone (simple cyanides) and with alkali and other metals (complex cyanides). Since the toxicity of cyanide to aquatic biota is related to the degree of dissociation of these complexes, analytical methods that distinguish between readily available and more stable forms of cyanide are used.		
Method Summary	<p>For total cyanide, a strong acid (H₂SO₄ or HCl-Hydroxylamine Hydrochloride) reflux distillation under vacuum is combined with an air purge to liberate hydrogen cyanide (HCN) from simple cyanides and most complex cyanides. The strong acid method uses strongly acid conditions (pH 2.0 to 4.0) to break down most strong metal-cyanide complexes as well as readily dissociable cyanide complexes and simple cyanides. All strong acid distillation methods can convert a small proportion of thiocyanate to free cyanide (normally < 1% conversion), but the HCl-HH method is designed to minimize this interference, and is intended for use with samples that may contain high levels of thiocyanate.</p> <p>For weak acid dissociable (WAD) cyanide, a weak acid reflux distillation under vacuum is combined with an air purge to liberate hydrogen cyanide (HCN) from simple cyanides and weakly bound complex cyanides. The WAD method utilizes a weak acid distillation solution (pH 4.5-6.0) along with zinc salts to minimize iron cyanide breakdown.</p> <p>With all the manual distillation cyanide methods, the resulting HCN gas is collected and trapped in a weak NaOH scrubbing solution. Applicable reference methods for these techniques are US EPA 335.4, APHA 4500-CN, and ASTM D2036.</p> <p>Laboratories may adopt alternative options to improve performance or efficiency provided that all stated performance requirements and prescribed (mandatory) elements are met.</p> <p>This method is performance-based. Distillation using a distillation apparatus is necessary for the use of this method, but various detection methods are permitted. Validate any apparatus being considered for use to demonstrate acceptable recovery of total cyanide before use - see performance requirements.</p>		
MDL(s) and EMS Analyte Codes	<u>Analyte</u>	<u>Approx. MDL (mg/L)</u>	<u>EMS Analyte Code</u>
	Cyanide, Total	0.001 – 0.005	0105
	Cyanide, Weak Acid Dissociable	0.001 – 0.005	0157
EMS Method Code(s)	<u>Method</u>		<u>EMS Method Code</u>
	Total Cyanide by H ₂ SO ₄ Distillation, Manual		0530
	Total Cyanide by HCl-HH Distillation, Manual		X324
	Weak Acid Dissociable Cyanide by Manual Distillation		X207
	***Refer to EMS Parameter Dictionary on the ministry website for all current EMS codes.		
Matrix	Freshwater, Seawater, Groundwater, Wastewater. Soil, Sediment, Sludge, and Solid wastes are applicable to this method after extraction by the BC MOE soil extraction method (Ref 6).		
Terms and Definitions	Total Cyanide: Total cyanide is an analytically defined term that refers to the sum total of all of the inorganic chemical forms of cyanide that dissociate and release free cyanide when refluxed under strongly acidic conditions. Total cyanide is determined analytically through strong acid distillation or UV radiation and exposure to strong acid followed by analysis of liberated free cyanide. In water, total cyanide includes the following dissolved		

species: free cyanide, weak metal cyanide complexes and strong metal cyanide complexes. However, it should be noted that some of the strong metal cyanide complexes, such as those of gold, cobalt and platinum, may not be fully recovered during the total cyanide analytical procedure (Ref. 5). Total Cyanide is also sometimes referred to as Strong Acid Dissociable (SAD) Cyanide.

Weak Acid Dissociable (WAD) Cyanide: An operationally defined group of cyanide species that undergo dissociation and liberate free cyanide when refluxed under weakly acidic conditions (pH 4.5-6). Weak acid dissociable cyanide is determined analytically through weak acid distillation and analysis of liberated free cyanide. Weak acid dissociable cyanide provides a conservative estimate of toxicity as it recovers both free cyanide and weak metal cyanide complexes (Ref. 5).

Interferences and Precautions

CAUTION: Use care in manipulating cyanide-containing samples because of toxicity. Process in a hood or other well-ventilated area. Avoid contact, inhalation, or ingestion. (APHA). Toxic HCN gas can be released from some cyanide species under acidic conditions.

Refer to reference methods for guidance for safe handling of reagents and distillation apparatus.

Refer to Reference 1, BC MOE Lab Manual method "Analysis of Cyanide (Total, Weak Acid Dissociable, and Free)" for a detailed list of applicable interferences.

Sample Handling and Preservation

Samples should be collected in plastic or glass bottles. The volume collected should be sufficient to ensure a representative sample, and to permit replicate analyses. Shield samples from UV light.

If samples are suspected to contain residual chlorine or other oxidizing agents, they must be treated with sodium arsenite or sodium thiosulfate at time of sampling. See "Residual Chlorine / Oxidizing Agents" in interference section of Reference 1.

i. If samples are suspected to contain sulfides, treat with lead acetate, lead carbonate, or cadmium carbonate (at time of sampling, if possible), to prevent the conversion of free cyanide to thiocyanate, and to prevent distillation of hydrogen sulfide. See "Sulfides" in interference section of Reference 1.

ii. If samples are suspected to contain aldehydes (above approximately 0.5 mg/L), or glucose or other sugars, add 2 mL of 3.5% ethylenediamine per 100mL of sample. See APHA 4500-CN B 3f for more details.

iii. Samples must either be analyzed within 24 hours of collection, or must be preserved with sodium hydroxide (target pH ≥ 12 ; pH ≥ 11 is acceptable) and cooled to $\leq 10^{\circ}\text{C}$ at the time of collection. Approximately 1 mL 6N NaOH per 250 mL sample is normally sufficient to achieve pH > 12 (highly buffered samples may require additional NaOH). All specified preservation techniques are ideally performed at time of collection, but may be conducted upon receipt at the laboratory within 24 hours of sample collection.

Stability

Samples: Holding time for NaOH preserved samples is 14 days when stored at $\leq 6^{\circ}\text{C}$ and shielded from UV light. Unpreserved samples must be analyzed or preserved within 24 hours.

Distillates: Ideally, distillates should be analyzed within 24 hours of distillation, but when stored at $\leq 6^{\circ}\text{C}$ and away from UV light, and with pH ≥ 11 , they may be held for up to 14 days prior to analysis.

Procedure

Detailed reagent and standard preparation and distillation procedures are not provided in this method, since they are specific to the equipment utilized. Appropriate procedures are described in the listed reference methods, and within manufacturer's manuals supplied with commercial systems. The procedures below are brief overviews of matrix elimination and detection steps used in the listed reference methods which include the mandatory elements of the test methods.

Distillation reagents: Detailed instructions for the preparation of reagents can be found in the EPA, APHA, and ASTM references (References 2, 3, and 4). The use of HCl-HH as a

total cyanide distillation reagent originates from References 7 and 8, and from prior versions of the BC lab manual (Ref. 10). The H₂SO₄ and HCl-HH methods are the same in terms of procedure and apparatus used, but the distillation reagents and reagent:sample ratios differ, as indicated below.

1. Strong Acid Distillation Method Reagents: The Sulfuric acid method recovers more Iron cyanide but is much more susceptible to SCN interference. The HCl-HH method has lower iron cyanide recovery but more effectively mitigates the thiocyanate interference. If in doubt, samples containing high levels of thiocyanate should be run by both methods to determine which method is more applicable.
 - a. H₂SO₄ Distillation Reagent - Sulfuric Acid, 18N: Prepare as per reference methods (References 2 and 3).
 - b. HCl-HH Distillation Reagent - Hydrochloric Acid: Hydroxylamine hydrochloride reagent (HCl-HH). Prepare in a 1 L class A volumetric flask by dissolving (100 ± 1) g NH₂OH-HCl in approximately 400 mL of deionized water. Slowly add (500 ± 10) mL of concentrated hydrochloric acid and dilute to 1 L with deionized water.
2. Weak Acid Dissociable Distillation Reagents:
 - a. Acetic Acid Solution (1.74 M). Example: Add 100 mL of glacial acetic acid to 900 mL of deionized water. Mix thoroughly.
 - b. Acetate Buffer. Example: Dissolve 410 g sodium acetate trihydrate (NaC₂H₃O₂ * 3H₂O) in 500 mL of deionized water. Add glacial acetic acid to yield a solution of pH 4.5.
 - c. Zinc Acetate Solution. Example: Dissolve 120 g Zn(C₂H₃O₂)₂*2H₂O in 500 mL of deionized water and dilute to 1 L.
3. Magnesium Chloride Solution. APHA Note: The requirement to use magnesium chloride in the distillation first appeared in the 15th Edition of Standard Methods. Review of data demonstrates that it is not essential. Use of magnesium chloride in the distillation is left to the discretion of the laboratory.
4. Sodium Hydroxide Solution: Make up an appropriate NaOH solution to be used as the absorber scrubber. Because the sensitivity of the colourimetric method is pH dependent, it is important to ensure that the pH of the absorber solution from any distillation procedure is adjusted to match the pH of the calibration standards.
5. Sulfamic Acid (NH₂SO₃H), crystalline (Strong acid methods only).
6. Methyl Red Indicator (WAD method only).

Distillation setup:

Set up reflux distillation apparatus as recommended by manufacturer. Distillations should be performed in an area with adequate ventilation and fume removal systems.

1. Mix sample well by shaking prior to dispensing the appropriate amount into a distillation vessel. Prepare any necessary dilutions using an appropriate sodium hydroxide solution (instead of deionized water).
2. Refer to manufacturer's instructions or guidance from the EPA or APHA methods (References 2, 3) for details on how reagents and samples are added to apparatus.
3. Dispense appropriate volume of NaOH scrubber solution into scrubbing vessel.
4. For Total Cyanide only: Add 2 g of sulfamic acid per 500 mL of sample (use proportionately less for smaller sample sizes). Ensure all sulfamic acid crystals are within the sample volume and not stuck in vessel or distillation apparatus.
5. Dispense the appropriate distillation reagent to maintain the following sample to reagent ratio:
 - a. Total CN by H₂SO₄: Use distillation reagent at a ratio of 1:10 (acid to sample).
 - b. Total CN by HCl-HH: Use distillation reagent at a ratio of 1:20 (acid to sample).
 - c. WAD CN: Acetate buffer 1:25, Zinc acetate solution 1:25 (reagent to sample).
6. For WAD Cyanide only: Add 2-3 drops methyl red indicator per 500 mL sample. If

solution does not stay pink add 1.74M acetic acid until pink colour persists (pH 4.5-6).

7. Turn on heating mantles or heater manifold. Heat samples until boiling and continue boiling for at least 1 hour.
8. After at least 1 hour of boiling, turn off the heating mantles and continue the airflow (under vacuum) for 5 minutes, allowing the samples to stop boiling.
9. Transfer each distillate to a well-marked plastic bottle.
10. If the quantitation of cyanide will not be conducted within 12 hours, store the distillates at $\leq 6^{\circ}\text{C}$. Distillates may be analyzed within 14 days if pH is ≥ 12 .
11. See BC MOE lab manual method Analysis of Cyanide (Total, Weak Acid Dissociable, and Free) for guidance on cyanide analytical method options.

Performance Requirements

Any analytical method options selected for this analysis must meet or exceed the performance requirements specified below.

Accuracy and Precision requirements are distinct from daily QC requirements, and apply to measures of long term method performance (averages and standard deviations). Achievement of these requirements is to be demonstrated during initial and ongoing method re-validation studies. For Initial Validations, averages of at least 8 Lab Control Samples or RMs must be assessed. Ongoing Re-validations (performance reviews) should assess QC data encompassing longer timeframes (e.g. 6 months to 1 year). A minimum frequency of 2 years is recommended for Ongoing Re-validations.

Accuracy Requirement: Laboratories must demonstrate method accuracy (measured as average recovery) of 80-120% for Lab Control Samples or Certified Reference Materials at concentrations above ten times the MDL. Complex cyanides such as potassium ferricyanide and simple cyanides like sodium or potassium cyanide must be evaluated.

Precision Requirement: Laboratories must demonstrate method precision equal to or better than 15% relative standard deviation for clean matrix spikes at concentrations above ten times the MDL.

Sensitivity Requirement: Where possible, the method should support Reporting Limits (and MDLs) that are less than 1/5 of applicable numerical standards. The method is not fit-for-purpose if an MDL exceeds a guideline, standard, or regulatory criteria against which it will be used for evaluation of compliance.

Quality Control

Summary of QC Requirements		
QC Component	Minimum Frequency	Minimum Data Quality Objectives
Method Blank (MB)	One per batch (max 20 samples)	Less than reported DL
Lab Control Sample (LCS)	One per batch (max 20 samples)	80 – 120%
Lab Duplicates (DUP)	One per batch (max 20 samples)	Waters: 20% RPD Soils: 30% RPD [or within 2x reported DL for low level results]
Matrix Spike (MS) or Reference Material (RM)	One per batch (max 20 samples)	70 – 130%
If DQOs are not met, repeat testing or report qualified test results. DQOs do not apply to MS results where sample background exceeds spike amount.		

Method Blank: Required, to evaluate laboratory contamination. Should be matrix-matched (same concentration of reagents as calibration and QC standards) and processed in the same manner as samples within the batch.

Laboratory Control Sample (LCS): Required, to evaluate laboratory method accuracy including matrix effects. Method spike or LCS must contain 50/50 mixture of KCN and FeCN spiking materials. KCN should be detected as Free CN, WAD CN, and SAD CN. FeCN should only be detected as Total (SAD) CN.

Matrix Spike: Required, to evaluate test method accuracy including matrix effects on individual samples. Sample Matrix Spikes must be spiked with a 50/50 mixture of KCN and FeCN spiking materials. KCN should be detected as Free CN, WAD CN, and SAD CN. FeCN should only be detected as SAD CN.

Prescribed Elements The following components of this method are mandatory:

1. Preservation protocols must be conducted as described. Samples must be analyzed or preserved with sodium hydroxide within 24 hours from time of sampling. Field preservation is strongly recommended unless laboratory treatment for interferences (e.g. sulfide) is necessary.
2. Stated sample holding times must be observed. Data must be qualified where holding times are exceeded.
3. Total CN only: Use 18N Sulfuric acid (H₂SO₄) distillation reagent with a ratio of 1:10 (acid to sample), or HCl-HH reagent at 1:20 ratio. The HCl-HH method is recommended for samples known to contain thiocyanate, to minimize false positive interferences.
4. WAD Only: Distillation shall be conducted using zinc acetate and acetate buffer solution at pH 4.5 to 6.0 as indicated by methyl red indicator solution.
5. Samples must be boiled for at least 1 hour using an appropriate vacuum purge apparatus setup (e.g. as described in EPA 335.4 or APHA 4500CN).
6. The pH of the absorber solution from any distillation procedure must match the pH of calibration standards for the determinative method.
7. QC requirements must be met as specified in the Quality Control section.

Apart from these limitations, and provided performance requirements are met, laboratories may introduce modifications to this method in order to improve quality or efficiency.

References

1. BC MOE Environmental Laboratory Manual method, Analysis of Cyanide (Total, Weak Acid Dissociable, and Free) – PBM.
2. EPA 335.4. Determination of Total Cyanide by Semi-automated Colorimetry, Rev 1. 1993. Reference for Manual distillation and semi-automated analysis.
3. APHA 4500 CN Cyanide, Approved 1999, Editorial 2011. Numerous references.
4. ASTM D2036 - Standard Test Methods for Cyanides in Water.
5. ASTM D6696-01. Standard guide for understanding cyanide species. Reference for terms and definition.
6. BC MOE Environmental Laboratory Manual method, Cyanide in Soils by Sodium Hydroxide Extraction – Prescriptive.
7. Csikai, N.J., Barnard, A.J., Determination of Total cyanide in thiocyanate containing wastewaters, Analytical Chemistry, 55, Vol. 11, 1983.
8. Conn, K., Cyanide Analysis in Mine effluent, cyanide and gold mining industry seminar, January 22, 1981.
9. US EPA Method 9016, Free Cyanide in Water, Soils, and Solid Wastes by Microdiffusion, Revision 0, June 2010.
10. BC MOE Environmental Laboratory Manual (2015), Cyanide; Strong Acid Dissociable (Hydrochloric Acid -Hydroxylamine Hydrochloride Method), revision date Dec 31, 2000 (replaced by this method in 2017).
11. BC MOE Environmental Laboratory Manual (2015), Cyanide – Weak Acid Dissociable (WAD), Distillation – PBM, revision date Oct 13, 2006 (replaced by this method in 2017).
12. BC MOE Environmental Laboratory Manual (2015), Cyanide – Strong Acid Dissociable (SAD), H₂SO₄ Distillation – PBM, revision date Oct 13, 2006 (replaced by this method in 2017).

Revision History

March 8, 2017 New method, combines and replaces previously existing BC Lab Manual methods for total cyanide by H_2SO_4 & HCl-HH distillations, and for weak acid dissociable cyanide by distillation. Refers to new lab manual method for cyanide analysis for analytical options.