Analysis of Cyanide (Total, Weak Acid Dissociable, and Free) - PBM

Parameter

Cyanide (Total, Weak Acid Dissociable, Free)

Analytical Method

Analysis of Cyanide Species (Total, Weak Acid Dissociable, Free)

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 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

This method is performance-based. Definitions and methodology requirements are provided for total cyanide, weak acid dissociable cyanide, and free cyanide. Detailed analytical conditions are not provided within this method, but suitable official reference method publications are referenced.

For information about manual distillation procedures that may be conducted prior to the use of this method, refer to BC Environmental Laboratory Manual method for Cyanide, Total or Weak Acid Dissociable, by Manual Distillation – PBM.

Analysis techniques that may be used with this method include manual or automated colourimetry, and automated flow systems (continuous flow analysis - CFA; or flow injection analysis – FIA) used with colourimetric or amperometric detection. Ion selective electrodes (ISE) may also be used where sensitivity is adequate for intended use.

Laboratories may adopt alternative options to improve performance or efficiency provided that all stated performance requirements and prescribed (mandatory) elements are met.

MDL(s) and EMS Analyte Codes

Analyte	Approx. MDL (mg/L)	EMS Analyte Code
Cyanide, Total	0.001 to 0.005	0105
Cyanide, Weak Acid Dissociable	0.001 to 0.005	0157
Cyanide, Free	0.001 to 0.005	code needed

Detection limits may vary by technique. ISE detection limits are higher (approx. 0.05 mg/L)

EMS Method Code(s)

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. 9).

Term 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. 1). 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. 1).

Free Cyanide: The form of cyanide that is bioavailable and known for its toxic effect on organisms. Free cyanide refers to either molecular hydrogen cyanide (HCN) or ionic cyanide (CN^-). At a pH of 7 or less in water, free cyanide is present entirely as HCN. Above pH 11, free cyanide exists entirely as CN^-. Free cyanide is operationally defined as being capable of diffusing as HCN gas at room temperature and at a pH of 6. Diffusible (free) cyanide is recovered and determined using microdiffusion (or gas diffusion) analysis (Ref. 1; Free Cyanide and Diffusible Cyanide).

Thiocyanate (SCN): Thiocyanate is not a cyanide species, and is not considered to be a component of total, WAD, or free cyanide, but it can be an interference with many methods for total cyanide (for most methods, thiocyanate causes interference on Total Cyanide of < 1% of the SCN concentration).

Total Cyanide + SCN: Some test methods measure the combined sum of Total Cyanide plus Thiocyanate. The Total Cyanide + SCN parameter may be used as a screening parameter for Total Cyanide standards, but cannot be used to confirm an exceedance of a Total Cyanide standard. Any test method that reports the sum of Total Cyanide + SCN must clearly state that both Total Cyanide and SCN are included.

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.

Several interferences are encountered with all cyanide methods. Known interferences include sulfides, aldehydes, thiocyanate, thiosulfate, carbonate, glucose and other sugars, and oxidizing agents such as chlorine. Most non-volatile interferences are eliminated or reduced by manual distillation, or by flash distillation or gas diffusion in automated methods.

When potentially complex samples are tested for the first time, prepare sample matrix spikes by fortifying with known amounts of cyanide to test for the presence of negative interferences, and to verify the suitability of chosen treatments for the removal of any interferences that are identified.

a. **Sulfides:** *Where necessary, it is preferred for sulfide treatment to be carried out before preservation, but it can be done after preservation.* Sulfides can interfere by two mechanisms:

   i. Oxidized products of sulfide rapidly convert cyanide to thiocyanate, especially at high pH (APHA). Therefore, if sulfides are present at time of NaOH preservation, free cyanide may not be detected by the method.

   ii. Hydrogen sulfide distills or is transmitted via gas diffusion with cyanide, and interferes with colourimetric, titrimetric, electrode, and amperometric detection methods. Testing for sulfide can be performed by placing a drop of sample on lead acetate test paper previously moistened with acetic acid buffer solution (pH 4). Darkening of the paper indicates presence of sulfide. If sulfide is present, add lead acetate, lead carbonate, or cadmium carbonate (Note: addition of too much lead acetate can reduce pH). Repeat test until a drop of treated sample no longer darkens the acidified lead acetate test paper. Filter sample, preferably before raising pH for stabilization.

      Note: If particulate metal-cyanide complexes are suspected to be present, filter solution before removing sulfide, and reconstitute sample by returning filtered particulates to the sample bottle after sulfide removal.

      Note: If sulfide removal cannot be done at time of sample collection, samples may be sent unpreserved to the laboratory for sulfide treatment within 24 hours of collection.

   iii. Lead acetate strip cannot detect sulfide at ppb levels.

   iv. Amperometric detection is especially sensitive to sulfide interference and requires use of inline bismuth nitrate or other suitable mitigation.

b. **Nitrite and Nitrate:**

i. **Total Cyanide:** High results may be obtained for samples that contain nitrate and/or nitrite. Nitrate and nitrite form nitrous acid that will react with some organic compounds to form oximes. Oximes will decompose under test conditions to generate HCN. The interference of nitrate and nitrite is eliminated by pretreatment with sulfamic acid. See reference methods for detailed guidance.

ii. **WAD and Free Cyanide:** Unlike for the measurement of total cyanide, nitrate and nitrite do not interfere with the measurement of WAD or free cyanide, therefore the addition of sulfamic acid is not required for these tests.

c. Residual Chlorine / Oxidizing Agents: Oxidizing agents such as chlorine can decompose most cyanide complexes. If residual chlorine or other oxidizing agents are suspected to be present, test a drop of the sample with potassium iodide-starch paper (KI-starch paper) at time of collection; a blue colour indicates the need for treatment (i.e. residual chlorine > 2 mg/L). If a bluish discolouration is noted, add 0.1 g sodium arsenite (NaAsO2) per litre of sample and retest. Sodium thiosulfate can also be used instead of sodium arsenite. Add small portions (0.02 g/L), with re-testing after each addition. Do not add excess sodium thiosulfate. To determine chlorine < 2 mg/L use a DPD colourimetric method (APHA 4500-Cl.G) and add a stoichiometric amount of sodium thiosulfate solution (APHA 4500- Cl.B.2*d*). Note: If the diagnostic test for sulfide is positive, oxidizing compounds are not expected.

d. Thiocyanate: SCN**-** can interfere as either a positive or negative bias depending on the conditions. SCN can be converted at high acidity in the presence of a strong oxidant to free cyanide. Conversely, a negative bias can occur when SCN is decomposed in the absence of oxidants, forming volatile carbonyl sulfide, which is converted to sulfide upon absorption in an alkaline liquid. For manual total cyanide distillation analysis use the BC MOE HCl-HH method (Ref. 13) to mitigate thiocyanate interference. To mitigate thiocyanate interference on flow systems (CFA or FIA), the use of a UV lamp and borosilicate glass reactor to deliver only wavelengths greater than 290 nm is necessary. 1% breakdown of SCN is an acceptable limit (Ref: ISO 14403-2, CALA Mar 2013 Challenge Sample Report). Analysis of a 25 mg/L SCN solution should yield < 1% conversion of Total Cyanide.

e. **Aldehydes:** Aldehydes (such as formaldehyde) convert cyanide to cyanohydrin which forms nitrile during distillation. This interference is not commonly associated with the analysis of mining effluent. See APHA 4500-CN B 3.f for interference check procedure.

Other published procedures for the removal or suppression of interferences may be employed provided they have been verified to be effective through the use of matrix spikes.

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.

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.

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 ≤ 10°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 prior to analysis when stored at ≤ 6°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 ≤ 6°C and away from UV light, and with pH ≥ 11, they may be held prior to analysis until up to 14 days from time of sampling.

Procedure

Detailed reagent and standard preparation and distillation/instrument 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, including the mandatory elements of each test method.

Preliminary Treatment:

Total cyanide matrix elimination techniques:

1. **Flow Analysis (CFA or FIA):** Complex bound cyanide is decomposed by Ultra Violet (UV) light in a continuously flowing stream at a pH < 3.8. A UV-B lamp (312 nm) and a decomposition spiral of borosilicate glass are used to filter out UV light with wavelength of less than 290 nm to limit the conversion of thiocyanate into cyanide. Hydrogen cyanide is separated by inline distillation at 125°C under vacuum OR by membrane gas diffusion at 30°C. Reference methods using this technique are ISO 14403-2, EPA Kelada, and ASTM D7511.
2. **Manual Distillation:** A strong acid (H_2SO_4 or HCl-HH) reflux distillation under vacuum is combined with an air purge to liberate hydrogen cyanide (HCN) from both simple and complex cyanides. The resulting HCN gas is collected and trapped in a weak NaOH scrubbing solution. Thiocyanate breakdown must be < 1% when distilling samples containing thiocyanate. Reference methods using this technique are EPA 335.4, APHA 4500-CN, ASTM D2036, BC MOE – H2SO4, and BC MOE HCL-HH.

WAD Cyanide (Weak Acid Dissociable) matrix elimination:

1. **Flow Analysis (CFA or FIA):** Hydrogen cyanide (HCN) is liberated in a continuously flowing stream at a slightly acidified pH of 4.5 to 6.0 and is separated by inline distillation at 120°C or membrane gas diffusion at 30 degrees. Strongly bound CN- complexes that would not be amenable to oxidation by chlorine are not converted. Iron cyanide complexes are precipitated with zinc sulfate. Reference methods using this technique are ISO 14403-2, and EPA Kelada. Ligand exchange methods such as ASTM D6888 may also be used.
2. **Manual Distillation:** A weak acid (pH 4.5 to 6.0) reflux distillation under vacuum is combined with an air purge to liberate hydrogen cyanide (HCN) from simple and easily dissociable cyanide complexes. The acetate buffer uses zinc salts to precipitate iron cyanide as a further assurance of the selectivity of the method. The resulting HCN gas is collected and trapped in a weak NaOH scrubbing solution. The reference methods for this technique is APHA 4500-CN- E.

Free Cyanide matrix elimination:

1. **Flow Analysis (CFA or FIA):** Hydrogen cyanide (HCN) is liberated in a continuously flowing stream at pH 6 and is separated by gas dialysis at room temperature into a pH 5.2 buffer stream. Methods using this technique are ASTM D7237 and ISO 17690:2015.
2. **Manual Gas Diffusion:** Sample preparation is carried out using a microdiffusion cell. 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 hours of diffusion. 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. The

reference method for this technique is EPA 9016.

Detection Techniques:

1. **Colourimetry.** Hydrogen cyanide is determined photometrically, based on the reaction of cyanide with chloramine-T to form cyanogen chloride. Cyanogen chloride subsequently reacts with isonicotinic acid and 1,3-dimethylbarbituric acid to yield a red coloured complex. The intensity of this colour is measured at 590-610 nm. Pyridine and barbituric acid may also be used but with a preferred wavelength of 575-582 nm. Note that pyridine has significant human toxicity; Refer to SDS before use. Reference methods using this technique are ISO 14403-2, APHA 4500-CN, and EPA 335.4.
2. **Amperometric Detection.** Hydrogen cyanide (HCN) gas diffuses through a hydrophobic gas diffusion membrane into an alkaline acceptor stream where the CN^- anion is captured and sent to an amperometric flow cell detector with a silver working electrode. In the presence of cyanide, the silver electrode surface is oxidized at the applied potential (Eapp = 0,0 V vs. the reference electrode). The anodic current measured is proportional to the concentration of cyanide in the standard or sample injected.
3. **Ion Selective Electrode (ISE):** CN^- in the alkaline distillate from the preliminary treatment procedures can be determined potentiometrically using a CN^- ion selective electrode in combination with a double junction reference electrode and a pH meter with an expanded millivolt scale, or a specific ion meter. This method can be used to determine CN^- concentration in the concentration range of approximately 0.05 to 10 mg/L CN^-. Refer to APHA 4500 CN F for more details. This method has limited sensitivity and is unsuitable for evaluation of aquatic life standards.

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 depending on the technique used:

All Cyanide Methods:

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. QC requirements must be met as specified in the Quality Control section.

4. All samples must be matrix matched with instrument calibration standards and QC for sodium hydroxide concentration.

5. For all Total Cyanide methods, labs must quantify the average degree of interference from Thiocyanate conversion (e.g. analyze a 25 mg/L solution of SCN and determine interference on Total Cyanide as a percentage of the SCN concentration). This information must be provided to clients on test reports (e.g. within methodology summaries).

6. For any test method that quantifies the sum of Total Cyanide + Thiocyanate, the test report must clearly indicate that both Total Cyanide and Thiocyanate are included.

Flow Analysis Methods (CFA or FIA):

Total Cyanide Analysis:

1. A UV reactor utilizing wavelengths greater than 290 nm and borosilicate reactor must be used (unless test results are reported as Total Cyanide + SCN).

2. Analysis of iron cyanide QC must demonstrate average recoveries greater than 80%.

WAD (Weak Acid Dissociable) Cyanide Analysis:

1. For colourimetric analysis, zinc sulfate reagent is used to precipitate out the iron cyanide in sample before distillation OR gas diffusion.

2. For amperometric methods using ligands, ligand exchange reagents must be added to samples prior to instrumental analysis.

3. For colourimetric analysis, the pH of the sample and digestion/distillation reagent before distillation OR gas diffusion is between pH 4.5 and 6.

4. UV reactors must not be used for WAD Cyanide.

Free Cyanide Analysis:

1. Prior to gas diffusion and analysis, the sample must be buffered to within the range of

pH 6.0 – 6.5.

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. ASTM D6696-01, Standard guide for understanding cyanide species. Reference for Terms and Definitions.
2. ISO 14403–2, Water quality - Determination of total cyanide and free cyanide by continuous flow analysis, 15 July 2012. Reference for colourimetric and in-line distillation techniques. Note that ISO 14403-2 defines Free Cyanide as cyanide species liberated at pH 3.8. This differs from the BC MOE definition, which uses pH 6.
3. APHA 4500 CN Cyanide, Approved 1999, Editorial 2011. Numerous references.
4. EPA 335.4, Determination of Total Cyanide by Semi-automated Colorimetry, Rev 1. 1993. Reference for manual distillation and semi-automated cyanide analysis.
5. EPA Kelada, Method Kelada-01 Kelada Automated Test Methods for Total Cyanide, Acid Dissociable Cyanide and Thiocyanate, Rev. 1.2 (1999).
6. ASTM D6888-04, Standard Test Method for Available Cyanide with Ligand Displacement and Flow Injection Analysis (FIA) Utilizing Gas Diffusion Separation and Amperometric Detection.
7. ASTM D7237-10. Standard Test Method for Free Cyanide with Flow Injection Analysis (FIA) Utilizing Gas Diffusion Separation and Amperometric Detection.
8. ISO 17690. Water quality - Determination of Available Free Cyanide (pH 6) using Flow Injection Analysis (FIA), Gas Diffusion and Amperometric Detection.
9. BC MOE Environmental Laboratory Manual, Cyanide in Soils by Sodium Hydroxide Extraction – Prescriptive.
10. ASTM D7511-12. Standard Test Method for Total Cyanide by Segmented Flow Injection Analysis, In-Line Ultraviolet Digestion and Amperometric Detection.
11. ASTM D2032-09 (2015). Standard Test Methods for Cyanides in Water.
12. BC MOE Environmental Laboratory Manual (2015), Cyanide Colour Development: Isonicotinic-Barbituric Acid Method, revision date Dec 31, 2000 (replaced by this method in 2017).
13. BC Environmental Laboratory Manual method for Cyanide, Total or Weak Acid Dissociable, by Manual Distillation – PBM.

Revision History

March 6, 2017	New method, replaces Cyanide Colour Development: Isonicotinic-Barbituric Acid Method, defines cyanide terms, and provides general guidance and requirements for all current MOE approved cyanide analysis techniques.