Laboratory Manager Approval: Kristy E. Hrehor / 08/19/2021

QA Manager Approval: Jeffney Moore / 08/19/2021

SW846 Method 9010C/9012B - Total Cyanide in Waste and Sediments-Manual Distillation with Automated Color Development

Access to this SOP shall be available within the laboratory for reference purposes; the official copy of this SOP resides on the official Georgia EPD website at https://epd.georgia.gov/about-us/epd-laboratory-operations. Printed copies of this SOP will contain a watermark indicating the copy is an uncontrolled copy.

1 Scope and Application

1.1 This method is a reflux-distillation procedure used to extract soluble cyanide salts and many insoluble cyanide complexes from wastes and leachates. It is based on the decomposition of nearly all cyanides by a reflux distillation procedure using a strong acid and a magnesium catalyst. Cyanide, in the form of hydrocyanic acid (HCN) is purged from the sample and captured into an alkaline scrubber solution. Method 9010 maybe used as a reflux-distillation procedure for both total cyanide and cyanide amenable to chlorination. The method is modified to use the MIDI-VAP 3000 and MIDI-VAP 4000 midi-cyanide distillation system and the Lachat Quickchem Auto-Analyzer.

1.2 Restricted Procedure
This procedure is restricted to use by an analyst experienced in the operation of the MIDI-VAP 4000 midi-cyanide distillation system and the Lachat Quickchem Auto-Analyzer. Additionally, the analyst must complete the requirements of the GAEPD Initial Demonstration of Analyst Proficiency prior to the analysis of actual samples. Analysts are further warned that performance of this analysis involves the use of potentially hazardous chemicals; refer to the GAEPD Chemical Hygiene Plan for additional information regarding chemicals required by this method.

2 Definitions

2.1 Refer to Section 3 and Section 4 of the Georgia EPD Laboratory Quality Assurance Plan (see SOP reference 13.4) for Quality Control Definitions.

2.2 Primary Source (PS) – A standard that is used to make up the calibration points of a curve.

2.3 Second Source (SS) – A standard made from a manufacturer other than that of the primary source.

2.4 Initial Calibration Verification (ICV) – An ICV is a second source standard that is used to verify the correctness of the primary source calibration curve. The ICV is run at a level equal to that of a Laboratory Control Sample (LCS) or the midpoint on the calibration curve.

2.5 Continuing Calibration Check (CCC) or Continuing Calibration Verification (CCV) – A standard used to verify that the response of the instrument has not changed since initial calibration. The CCC is run at a level equal to that of a Laboratory Control Sample (LCS) or the midpoint on the calibration curve.

2.6 Calibration Blank (CB), Initial Calibration Verification Blank (ICB), Method Blank (MBLK), MDLB (MDL Blank) or Continuing Calibration Blank (CCB) – A volume of reagent water fortified with the same matrix as the calibration standards, but without the analytes.

2.7 MDLS (Method Detection Limit Spike) – MDLB spiked with analytes at the lowest calibration level to be used for the determination of MDL.

2.8 LCS (Laboratory Control Sample) and LCSD (Laboratory Control Sample Duplicate) are prepared by spiking laboratory reagent water, Ottawa sand or air sampling device with the target analyte or compound. They are used to validate the analytical batch with respect to accuracy and precision.

3 Interferences

3.1 Interferences are eliminated or reduced by using the distillation procedure. Chlorine and sulfide are interferences.

3.2 Oxidizing agents such as chlorine decompose most cyanides. Chlorine interferences can be removed by adding an excess of sodium arsenite to the waste prior to preservation and storage of the sample to reduce the chlorine to chloride, which does not interfere. Ascorbic acid can be used as an alternative although it is not as effective as arsenite.

3.3 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. All standards must be pre-treated with the added bismuth nitrate and sulfamic acid (see 3.4) and distilled in the same manner as the sample if sulfide is present. Note: The addition of bismuth nitrate to the samples and standards increases the nitrate concentration, therefore, sulfamic acid also has to be added.

3.4 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 eliminated 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.

3.5 Thiocyanate is reported to be an interference when present at very high levels. Levels of 10 mg/l were not found to interfere in Method 9010.

3.6 If fatty acids, detergents, surfactants, and other compounds cause foaming during the distillation, refer to Sec. 6.7 of SOP Reference 13.2 for the extraction procedure to eliminate this interference.

4 Safety

4.1 Refer to the EPD Laboratory Safety / Chemical Hygiene Plan & Fire Safety Plan, online revision. (SOP Reference 13.10)

5 Apparatus and Equipment

5.1 Sample Container: Samples are collected in wide mouth 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.

5.2 Plastic culture tubes, O.D. x L: 13mm x 100mm, Fisher Scientific part # 14-956-8E or equivalent or glass culture tubes 12mm x 75 mm VWR part # 60825-502 or equivalent.

5.3 Glassware – Class A volumetric flasks, graduated cylinders and pipettes

5.4 Midi Distillation System with integrated heater, water and vacuum manifolds, timer, tubing and connectors, and reflux glassware designed for cyanide distillation.

5.5 Lachat Quikchem flow injection analysis instrument

5.5.1 Lachat XYZ Auto-sampler

5.5.2 Auto-sampler racks (90 position)

5.5.3 Reagent pump

5.5.4 Reaction unit or manifold

5.5.5 Colorimetric detector with 570 nm interference filter

5.5.6 Computer with Microsoft Windows operating system with Lachat Omnion software or equivalent

5.6 Vacuum source and water source for Midi Distillation system

5.7 Vacuum source for degassing mobile phases

5.8 Flow cell: 10 mm path length, 80 µl, glass

5.9 500 ml excess cyanide trap

5.10 Air displacement pipettes of various volumes, auto- pipettor, pipette tips in various sizes. Air displacement pipettes and auto-pipettors may also be described as mechanical pipettes.

5.10.1 Each day of use, the volume dispensed by each mechanical pipette must be verified for the specific volume for which the pipette is being used.

5.10.1.1 Mechanical pipette volumes are verified by measuring the weight of a volume of water dispensed by the unit. At room temperature, 1 ml of water is equal to 1 g. Mechanical pipettes must be verified to be within ± 2.5% of the expected weight.

5.10.1.2 Auto-pipettors may be verified by measuring the volume dispensed with a graduated cylinder. The volume dispensed must be within ± 2.5 percent of the nominal volume.

5.10.1.3 Mechanical pipettes must be professionally calibrated every 6 months.
5.11 Balance: analytical, capable of accurately weighing to the nearest 0.0001g.
5.12 Disposable transfer pipettes:
5.12.1 Plastic - VWR® Disposable Transfer Pipets PN # 16001-190 or Fisherbrand™ Standard Disposable Transfer Pipettes PN # 13-711-7 M
5.13 50 ml Centrifuge Tubes: For standards. VWR Part Number 21008-240, or equivalent
5.14 Nitrate-Nitrite test strips:
5.14.1 HACH – Catalog # 27454-25 or equivalent.
Expiration date one year from date of receipt if no expiration date given.
5.15 Lead Acetate Paper:
5.15.1 Key Scientific – Catalog # K375(Fisher # NC9506930) or equivalent.
Expiration date one year from date of receipt if no expiration date given.
5.16 Potassium Iodide Starch Test paper:
5.16.1 Fisher Scientific -Catalog # NC0931813 or equivalent
Expiration date one year from date of receipt if no expiration date given.
5.17 Dilu-vials
5.17.1 VWR 20 ml Blood cell-counter vials, polystyrene with caps VWR#14310-684
5.18 Boiling chips:
5.18.1 Chemware Ultra-Pure PTFE Boiling Stones – Item # 0919120 or equivalent
5.19 Sand:
5.19.1 EMD Millipore– Catalog # SX0070-1 or equivalent.
5.20 Spatulas – for mixing sample
5.21 Narrow range pH paper – Fisherbrand Item # 13-640-514 pH Paper 12.5-14.0 or equivalent.
5.21.1 Expiration date one year from date of receipt if no expiration date given.
5.22 50 ml centrifuge tubes

6 Reagents

6.1 Reagent Water:
6.1.1 Purified water which does not contain any measurable quantities of target analytes or interfering compounds for each compound of interest (Deionized, HPLC, Milli-Q water, or equivalent. Milli-Q water has a resistivity of 18.2[MΩ.cm]@ 25ºC and a TOC of 50 ug/L or less).
6.2 Carrier, 0.25N Sodium Hydroxide Solution(0.00 ug/kg CN standard/CCB/ICB/MBLK/MDLB):
6.2.1 Dissolve 10 g NaOH in reagent water and bring to volume in a IL volumetric flask, or dissolve 40 g of 50% NaOH in reagent water and bring to volume in a 2 L volumetric flask. Prepare several liters as one batch to be used for carrier and standards. Prepare every two weeks.
6.2.2 The sand used for the MBLK/MDLB must be stored in a sample collection container prior to use. Record lot # of container used.
6.3 Magnesium Chloride reagent, 51 % w/v):

6.3.1 Dissolve 51 g $MgCl_26H_2O$ in reagent water and dilute to volume in 100 ml volumetric flask.
6.3.2 Reagent is stable for 3 months.
6.4 Sulfuric Acid, 18N:
6.4.1 Slowly add 50 ml of concentrated H_2SO_4 to 50 ml of reagent water.
6.4.2 Reagent is stable for 3 months.
6.5 Lead Acetate Paper:
6.5.1 Sulfide indicator paper (see 5.15)
6.6 Potassium Iodide Starch Paper:
6.6.1 Oxidant indicator paper (see 5.16)
6.7 Nitrate test strips:
6.7.1 HACH – Catalog # 27454-25 or equivalent.
6.7.2 Expiration date one year from date of receipt if no expiration date given.
6.8 Chloramine-T (CAS 127-65-1):
6.8.1 Dissolve 2 g of chloramine-T hydrate in 500 ml volumetric flask and dilute to volume with reagent water. Prepare daily. It is recommended that this chemical be discarded six months after opening because it is an air sensitive solid.
6.9 Pyridine-Barbituric Acid:
6.9.1 In the fume hood, place 15g of barbituric acid (CAS 67-52-7) in a 1L volumetric flask and add 100 ml of reagent water, rinsing down the sides of the flask to wet the barbituric acid. Add 75ml of pyridine(CAS 110-86-1) while stirring and mix until the barbituric acid dissolves. Add 15 ml concentrated hydrochloric acid (HCl), mix and cool to room temperature. Dilute to volume with reagent water. Prepare fresh weekly.
6.10 0.71M Phosphate Buffer
6.10.1 Add 97 g of Potassium Phosphate Monobasic, anhydrous, (KH_2PO_4)(7778-77-0) in a 1L volumetric flask and dilute to volume with reagent water. Prepare fresh monthly.
6.11 Ascorbic Acid: Crystal(CAS 50-81-7):
6.11.1 If oxidizing agents are present.
6.12 Sulfamic Acid (CASRN 212-57-3):
6.12.1 If nitrate/nitrite concentration is $\geq$10.0 mg/L or if bismuth nitrate is added.
6.13 Glacial Acetic Acid (CH_3COOH):
6.14 Bismuth Nitrate (0.062M)(CAS 10035-06-0):
6.14.1 Dissolve 30 g of Bismuth Nitrate ($Bi(NO_3)_3{\cdot}5H_2O$) in 100 ml of reagent water. While stirring, add 250 ml of glacial acetic acid (CH_3COOH). Stir until dissolved and dilute to 1 liter with reagent water.
6.14.2 Prepare fresh every 6 months.
6.15 Cyanide Stock Standard A, 1000 mg CN/L:
6.15.1 This standard is purchased from a commercially available source. This purchased standard is stable until expiration date on bottle or within 14 days of opening date, whichever is sooner.
6.16 Cyanide Stock Standard B, 10 mg CN/L:
6.16.1 Pipette 5 ml Cyanide Stock Standard A in a 500 ml volumetric flask. Dilute to mark with 0.25N NaOH and mix. Standard is good for 14 days.

6.17 Calibration Standards:

6.17.1 8 levels of calibration standards are prepared by the addition of aliquots of Cyanide Stock Standard B(10 mg CN/L) to Carrier, (0.25N Sodium Hydroxide Solution) as follows:

Table 6.17.2 – Working Cyanide Standards

Cyanide Stock B (10 mg/L) (mL)	Final Volume Carrier (.25N NaOH) (mL)	Cyanide Concentration (CNTALS) (ug/kg)
NA	1 L	0
2 ml	1 L	1000
1 ml	200 ml	2500
2 ml	200 ml	5000
4 ml	200 ml	10000
6 ml	200 ml	15000
8 ml	200 ml	20000
10 ml	200 ml	25000

6.17.2 Standards are stable for 14 days.

6.18 ICV Cyanide Stock Solution(see 2.4) or Second Source(SS):

6.18.1 ICV Cyanide Stock Solution (1000 mg/L):

6.18.2 The ICV stock standard is typically a standard intended as a “QC Sample” but used as a second source standard instead.

6.18.3 This stock standard must be from a different source than the stock standard used to make the calibration standards.

6.18.4 This standard is purchased from a commercially available source. The purchased standard is stable until expiration date on bottle or within 14 days of opening date, whichever is sooner.

6.19 ICV Intermediate Cyanide Solution (10 mg/L):

6.19.1 A 1 ml aliquot of the ICV Cyanide Stock Solution(1000 mg/L) is pipetted into a 100 ml volumetric flask and diluted to volume with Carrier, 0.25N Sodium Hydroxide Solution(see 6.2).

6.20 ICV Cyanide Solution (0.300 mg/L or 300 ug/L):

6.20.1 A 3 ml aliquot of the ICV Cyanide Intermediate Stock Solution(10 mg/L) is pipetted into a 100 ml volumetric flask and diluted to volume with Carrier, 0.25N Sodium Hydroxide Solution(see 6.2).

6.20.2 The ICV solution is stable for 14 days.

6.21 1N NaOH solution:

6.21.1 Dissolve 20 g NaOH in reagent water and bring to volume in a 500 ml volumetric flask. Prepare fresh every 6 months.

6.22 50% Sodium Hydroxide Solution:

6.22.1 Commercially available.

6.23 Sand:

6.23.1 EMD SX0070-1 or equivalent .
6.23.2 Purchased from a commercially available source.
6.23.3 The purchased standard is stable until expiration date on bottle or within 2 years of opening date, whichever is sooner.

7 Sample Collection

7.1 Samples are collected in wide mouth glass or plastic containers that are amber in color or are covered with aluminum foil.
7.2 Samples are stored at 0 - 6º C (not frozen).
7.3 Sample holding time is 14 days.
7.4 Aqueous sample must be preserved by adding 50% sodium hydroxide solution until the pH is greater than or equal to 12 at the time of collection.

8 Calibration

8.1 Calibration Standards
The calibration curve consists of the calibration standards at the following concentrations: 0.00 µg/kg CN, 1000 µg/kg CN, 2500 µg/kg CN, 5000 µg/kg CN, 10000 µg/kg CN, 15000 µg/kg CN, 20000 µg/kg CN and 25000 µg/kg CN for Hazardous Waste samples when the CNTALSED analysis code is requested.

8.2 Calibration Curve:
8.2.1 The Lachat Quickchem is calibrated daily. Eight standards are used to construct the CN calibration curve. Minimum acceptable correlation coefficient, r, is $r \geq 0.995$ using a linear regression.
8.3 Calibration verification:
8.3.1 An initial calibration verification standard (ICV), continuing calibration check standard (CCC), Method Blank (MBLK) and an initial calibration blank (ICB) must be analyzed immediately after the calibration standards.
8.3.2 The ICV standard must be prepared with a stock from a different source than the standards used in the calibration of the instrument.
8.3.2.1 The % Drift (see calculation 11.6) of the ICV from the true value must be within ± 10%. Repeat once if it fails. If it fails the second attempt, determine the source of the problem, correct and recalibrate.
8.3.3 The ICB and MBLK values must be less than the method RL or the run will have to be repeated. The CCB value must be less than the method RL or the samples associated with the out of control CCB will have to be reanalyzed.
8.3.3.1 The MBLK must be distilled.
8.3.3.2 The ICB is not distilled
8.3.4 A CCC and a Continuing Calibration Blank (CCB) must be analyzed every 10 samples and at the end of the sample run and must meet the same criteria as the ICV and ICB respectively.
8.3.4.1 If the CCC or CCB do not meet acceptance criteria, then all samples affected by the out of control CCC or CCB are to be rerun.

8.3.4.2 The CCC may be from the same source as the calibration standards.

8.4 A low level standard (1000 ug/kg) must be distilled and analyzed once per analytical run. Recovery of the standard must be ± 50% of expected value.

8.5 A high level standard (20,000 ug/kg) must also be distilled and analyzed once per analytical run. Recovery of the standard must be within 10% of its expected value.

8.6 A MDLS (low level mdl spike) at the concentration of 1000 ug/kg must be analyzed with each batch to perform an ongoing MDL study. All batch QC must be valid to report this result**.** The low level digested standard can be poured up as MDLS. They don't need to be digested separately.

8.6.1 The sand used for the MDLS must be stored in a sample collection container prior to use. Record lot # of container used.

8.7 A MDLB (MDL blank) must be analyzed once per analytical batch to perform an ongoing MDL study. All batch QC must be valid to report this result.

8.7.1 The sand used for the MDLB must be stored in a sample collection container prior to use. Record lot # of container used.

9 Quality Control

9.1 Refer to Table 14.1 for Reporting Limits (RL's), Appendix A, Table A.1 for Quality Control Acceptance Criteria, and Table 14.2 for Quality Control Procedures associated with this method.

9.2 See SOP reference 13.7 for control charting procedures.

9.3 See SOP reference 13.6 for training certification procedures.

9.3.1 For Initial Demonstrations of Capability (IDC), SW846 Method 9010C/9012B requires a recovery range of 85% - 115% for CN (see calculation 11.8).

9.3.1.1 The EPD Laboratory sets a 30% RSD requirement for IDC replicates (see calculation 11.4).

9.3.2 The EPD Laboratory uses the most current accuracy and precision control ranges in use for samples for Continuing Demonstrations of Capability (CDC). If 4 replicates are performed (as opposed to two LCS/LCSD pairs) a 30% RSD is required (see calculation 11.5).

9.4 Control Limits:

9.4.1 The default control limits from SW846-9010C/9012B are 85 – 115% recovery for Total Cyanide for LCS recoveries as determined by the EPD Laboratory. The EPD Laboratory applies LCS recovery limits to LCSDs. Note, unless specified by method, the EPD Laboratory does not validate batch quality based on LCSD recoveries.

9.4.2 By default, the EPD Laboratory sets LCS/LCSD precision control limits to be 0 – 30% RPD.

9.4.3 LCS/LCSD recovery and precision control limits are static as determined by the EPD Laboratory.

9.4.4 10% of all routine samples must be spiked. SW846 does not specify matrix spike recovery control limits; therefore the MS/MSD recovery limits are 85 – 115%. These limits are static.

9.4.5 By default, the EPD Laboratory sets default MS/MSD precision control limits to be 0 – 30% RPD. MS/MSD precision limits are static as determined by the EPD Laboratory.

9.4.6 See Administrative SOP for Control Charting and Control Limits for further details.

9.4.7 Batch samples in groups of 20. For each batch, analyze a Matrix Spike (MS) and a Matrix Spike Duplicate (MSD) for a minimum of 10% of routine samples.

9.4.8 For batches of 1 to 10 routine samples, one MS/MSD pair must be spiked. For batches of 11 to 20 routine samples, two MS/MSD pairs must be spiked using different samples for each pair. Additional MS/MSD pairs may occasionally be required in order to meet the 10% requirement.

9.4.9 In-house limits based on control charts may never exceed the default limits.

9.4.10 See Administrative SOP for Control Charting and Control Limits, SOP reference 13.7 for further details.

9.5 MDL Studies:

9.5.1 MDL (method detection limit) is the minimum concentration of a substance that can be measured and reported with 99% confidence that the value is above zero.

9.5.1 The actual MDL varies depending on instrument and matrix.

9.5.2 The MDL must be determined annually for each instrument prior to results being reported for that instrument. The MDL determined for each compound must be less than the reporting limit for that compound.

9.5.3 The Method Detection Limit Study for all analytes must be performed initially on a new instrument and performed after major instrument repairs or changes to procedures. There are two ways to perform the MDL. The first is with 7 samples and 7 blanks over 3 separate days. The second preferred way the MDL is run as a continuous format.

9.5.4 The 7 MDL samples study is performed by preparing 7 spiked vials, MDLSpike, spiked at the lowest calibration point of the curve, and preparing 7 clean blank vials filled with DI water, MDLBlank. These 7 sets of spiked and blank vial "pairs" are analyzed over 3 separate days, there may or may not be a non-analysis day between each of the 3 days. A total of 14 vials are prepared, 7 spiked and 7 blank.

9.5.5 A continuous format MDL study is performed where one vial is spiked as an MDLSpike, at the lowest point of the calibration curve and analyzed with every batch of samples along with the method blank vial as an MDLBlank.

9.5.6 For Drinking Water, WPCP and Water Quality Samples, the results of the MDLBlank will be entered into Labworks using the Method Blank test code, B_CNTALSED. The MDLSpike result will be entered using the MLCNTALSED. The MDL Spiked Amount will be entered into the test code MACNTALSED. The instrument used for the MDL and Blank analysis will be selected using the test code INSTR-CNTALSED.

9.5.7 MDL study must be performed every six months and before the MDL for the instrument expires.
9.5.8 MDL data is pulled from a two year period.

10 Procedure

10.1 Procedure for Distillation
10.1.1 Remove sample containers, standards and reagents from cold storage and allow equilibration to room temperature prior to sample preparation and/or analysis.
10.1.2 Air displacement and other mechanical pipetters must have the delivery volume verified each day of use for each specific volume for which the device is used on that day.
10.1.3 Make sure to alternate positions of the QC samples each run to ensure all spaces on the distillation units are working properly.

10.2 Interference check
10.2.1 Pour off top layer of liquid (if present) and then mix sample well with a spatula. Weigh out 1.00-1.05 grams of sample into a 50 ml centrifuge tube and add 50 ml of 0.25N NaOH solution. Vortex to mix.
10.2.2 Use lead acetate paper to check the sample for the presence of sulfide.
10.2.2.1 A positive test is indicated by a black color on the paper. See section 10.3.9.1 for sample pretreatment procedure.
10.2.3 Check for oxidant presence with potassium iodide starch test paper.
10.2.3.1 A positive test is indicated by a dark blue color on the paper. See section 10.3.9.3 for sample pretreatment procedure.
10.2.4 Check for presence of nitrate/nitrite using Nitrate/Nitrite test strips.
10.2.4.1 If there is a presence of nitrate and or nitrite of 10 mg/L or greater, the sample will have to be pretreated. See section 10.3.9.2 for sample pretreatment procedure.

10.3 Distillation sample prep
For samples, add 2 or 3 boiling chips to the back reflux flask. Then add 1.00-1.05 grams of soil sample to the flask. Next pour 50 ml of 0.25N NaOH solution, using a class “A” graduated cylinder, to the sample to the flask. Mix on vortex mixer until soil is uniformly suspended.
10.3.1 For LCS and LCSD’s, add 2 or 3 boiling chips to the back reflux flask. Pipette 1.5 ml of 10 mg/L CN Stock Solution B to spike at 15000 ug/kg directly to the boiling chips(See Section 11.8 for calculation). Then add 1.00-1.05 grams of commercially prepared sand, that has been stored in a sample collection container, to the flask. Finally add 50 ml of 0.25N NaOH to the flask. Mix on vortex mixer until soil is uniformly suspended. Make sure to alternate positions of the LCS and LCSD for each run to ensure all spaces on the distillation units are working properly. Record lot # of sample container.

10.3.2 For MS and MSD's, add 2 or 3 boiling chips to the back reflux flask. Pipette 1.5 ml of 10 mg/L CN Stock Solution B to spike at 15000 ug/L directly to the boiling chips. Then add 1.00-1.05 grams of soil sample to the flask. Finally add 50 ml of 0.25N NaOH solution, using a class "A" graduated cylinder, to the sample to the flask. Mix on vortex mixer until soil is uniformly suspended. Make sure to alternate positions of the MS and MSD for each run to ensure all spaces on the distillation units are working properly.

10.3.3 The sand for the CCB/MBLK/MDLB must be stored in a sample collection container before it is placed into the appropriate flask. Record lot # of container used.

10.3.4 The sand for the MDLS 1000 mg/kg standard must be stored in a sample collection container before it is placed into the appropriate flask. Record lot # of container used.

10.3.5 Add 50 ml of 0.25N NaOH to the front absorber flasks using a class "A" graduated cylinder.

10.3.6 Connect the a) reflux flask, b) reflux impinger with air inlet and c) cold finger condenser, and the d) absorber flask, and e) absorber impinger in order. Put the excess cyanide trap containing 250 ml 1.0 N NaOH in the vacuum line.

10.3.7 Turn on water and set flow meter at 10. (Water flow meter is located on the left side of the Midi-Dist unit).

10.3.8 Start a slow stream of air entering the reflux flask by adjusting the vacuum needle valves until approximately 1 air bubble/second enters the reflux flask. This air rate will carry HCN gas from the reflux flask to the absorber flask and usually will prevent a reverse flow of HCN through the air inlet. If this air rate does not prevent sample backup in the delivery tube, increase the airflow rate to 2 or 3 bubbles per second. Maintain airflow throughout the reaction.

10.3.9 Pretreatment of samples containing interferences

10.3.9.1 If a sample is known or suspected to contain sulfide, batch the sample by itself, and digest and analyze it on a separate run. All standards and QC have to be digested and pre-treated with bismuth nitrate and sulfamic acid. To pretreat samples, standards and QC, add 5.0 mL of 0.062M bismuth nitrate through the air inlet tube of the sample. Mix for three minutes. Check a drop of sample and if sulfide is still present, then "J" flag and comment on sample. Next add 0.2 g of sulfamic acid solution through the air inlet tube of the sample and let mix for three minutes.

10.3.9.2 If there is a presence of nitrate and or nitrite of 10 mg/L or greater in a sample, add 0.2g of sulfamic acid through the air inlet tube of the sample, the method blank, the low level standard (1000 ug/kg), the high level standard (20,000 ug/kg), and the LCS and LCSD. Rinse with reagent water. Let mix for 3 minutes prior to the addition of 18 N Sulfuric Acid.

10.3.9.3 If there is a presence of oxidants, add a few crystals of ascorbic acid to the stabilized sample (pH $\geq$ 12), a few crystals at a time until a drop of sample produces no color on the indicator paper. Then add an additional 0.6 g of

ascorbic acid per liter of sample volume. Note: For soil samples, the sample must be pretreated in the field.

10.3.10 Slowly pipette 5 ml of 18 N Sulfuric Acid through all air inlet tubes. Let mix for 3 minutes.

10.3.11 Pipette 2.0 ml of magnesium chloride reagent through all the air inlet tubes. Rinse tubes with reagent water and let mix for 3 minutes.

10.3.12 Switch on power to the distillation system and set timer to 105 minutes. Temperature is set at 126ºC and will permit rapid boiling. Do not flood condenser inlet or permit vapors to rise more than halfway into condenser. Adequate refluxing is indicated by a reflux rate of 40 to 50 drops/minute from the cold finger condenser bottom. To ensure adequate airflow rate, unit needs to be monitored carefully until samples reach boiling point.

10.3.13 Reflux for at least 1 hour. Turn off power, but continue air flow for 15 minutes. Close vacuum source and remove absorber flask when cool. Allow any absorber solution to drain from absorber head back into absorber tube.

10.3.14 Make sure to measure the temperature of the distillation system each day it is used by placing a certified thermometer probe into a distillation tube containing sand. Turn on the distillation heating block and let it get to the programmed temperature. Record the temperature on distillation log. Make sure to alternate positions of this temperature check tube for each run to ensure all spaces on the distillation units are working properly. This temperature check can be done in the morning while the samples are being prepped or it can be done while digesting if space is available. The optimal temperature is 126 ± 10ºC.

10.4 Procedure for Analyzing Samples using the Lachat

10.4.1 Turn on the computer, instrument, auto-sampler and pump.

10.4.2 Check tubes for wear. Replace as needed. Tighten down the platens on the tubes. Make sure to only clamp down the platen on the tubes for the Cyanide method. The rest of the tubes can remain loose. Also make sure the CN waste line is placed securely in the CN waste container. Caution: Do not mix CN waste streams with ammonia or nitrate waste streams.

10.4.3 Place all lines in reagent water. Start the pump by pressing the Manual Run/Stop button on the pump. Pump speed should be 35. Check for leaks, or backpressure by pulling each line out one at a time to monitor flow through the line. The flow should not fluctuate.

10.4.4 Click on Open icon and make sure you are in the Cyanide method directory. Choose the CNTALSED that was analyzed using that method.

10.4.5 The screen prompt will ask if you want to change the set point of the relevant heater. Click yes. Make sure all lines are pumping water before you do this or you could melt the tubing surrounding the heater.

10.4.6 Type the samples in the sample worksheet. Make sure to click enter after each entry or the new entry will not update.

10.4.7 Once all samples are typed in the worksheet, click on the Run icon and then click on export worksheet data. Make sure to place a copy of this worksheet in the run log.

10.4.8 Degas all reagents and then place labeled lines into the appropriate reagents and make sure flow is still correct.

10.4.9 Load your standards in the standard rack, putting your highest standard in the first position. Then load samples in the sample tray according to your numbered batch sheet.

10.4.10 After the reagents have been pumping for about 5 minutes, click on the Preview icon to view baseline and make sure it is stable. Record baseline value in maintenance log and that you checked pump tubes. Record any other maintenance performed on the instrument.

10.4.11 Click on the Start Icon to start the run, once all samples and standards have been loaded.

10.4.12 After the calibration is complete, verify that the correlation is 0.995 or better and that the zero standard area count is less than the lowest standard area count. If so, then let the run proceed.

10.4.13 When the run is finished, click on the Tools icon and then click on Custom Report. Then click on the print icon.

10.4.14 Dilute all samples for which the responses are greater than the high standard. Dilutions should be performed after distillation.

10.4.14.1 Note: If a sample chosen as a QC sample is off-scale, dilution after distillation will also dilute the spike concentration causing MS/MSD recovery failure. Initiate a corrective action. Diluting the sample prior to distillation does not provide enough sample volume to constitute a representative sample.

10.4.15 Volumes and amounts of reagents, chemicals and standards may be altered as long as the final concentrations remain the same. Sample volumes and injection amounts may be altered as long as required detection limits can be met and sample/reagent ratios remain the same.

10.5 Shutdown Procedure

10.5.1 When the run is finished, place all lines in reagent water. Let the reagent water run through the lines for 5 minutes.

10.5.2 Exit from the user screen by clicking on the Run icon and then click yes when requested to exit Omnion.

10.5.3 Click on the start icon at bottom of the screen, and then select turn off computer icon and then click on Turn off icon. The computer will now shut down.

10.5.4 After the lines have been pumping reagent water for 5 minutes, place them in an empty beaker and pump air for about 5 minutes or until dry. Make sure the heater is off at this time so the tubing will not melt.

10.5.5 Make sure to dispose of Cyanide waste in the properly labeled 5 gallon analysis waste container. When full, the containers need to be placed in the chemical storage building and the receiving lab supervisor needs to be notified.

10.5.6 Make sure to cap analysis waste container when not in use.

10.6 Procedure for determining % solids for non-waste soils
* Note: This procedure is only needed if it has not already been completed by the Organic laboratory.
10.6.1 Refer to SOP 3-044 Percent Solids if needed.
10.6.2 Be sure to calculate the final MDL by using equation in Section 11.12 or use the Excel worksheet "cn_mdl calc solids performed temp ugKg.xls."

11 Calculations

11.1 A standard curve is prepared by plotting the absorbance value of standards versus the corresponding cyanide concentration. The concentration of cyanide in the sample digestate is determined by plotting sample absorbance against the standard curve. Calculation of final result is accomplished using the following equation:

$$\text{CN ug/kg} = \frac{(X)(Y)}{(kg)}$$

11.1.1 Where:
X = concentration in NaOH trapping solution in ug/L
Y = Volume (in liters) of the trapping solution
kg = weight (in kg) of the sample (wet weight)

11.2 Mean ($\overline{X}$):

$$\overline{X} = \frac{X_1 + X_2 + \cdots X_n}{n}$$

11.2.1 Where:
$X_1 + X_2 + \cdots X_n$ = The sum of a set of values X_i, i = 1 to n
n = The number of values in the set

11.3 Standard Deviation (n – 1) (σ_{n-1}):

$$\sigma_{n-1} = \sqrt{\sum_{i=1}^{n} \frac{(X_i - \overline{X})^2}{n-1}}$$

11.3.1 Where:

$\overline{X}$ = Mean of the values
X_i = Individual values 1 through i
n = Number of values

11.4 Percent Relative Standard Deviation (%RSD):

$$\%RSD = \frac{\sigma_{n-1}}{\overline{X}} * 100$$

11.4.1 Where:

σ_{n-1} = Sample Standard Deviation
$\overline{X}$ = Mean of the values

11.5 Relative Percent Difference (%RPD or RPD):

$$\%RPD = \frac{|X_1 - X_2|}{\frac{(X_1 + X_2)}{2}} * 100$$

11.6 Percent Drift, %Drift:

$$\%Drift = \frac{(Concentration_{Calculated} - Concentration_{Expected})}{Concentration_{Expected}} * 100$$

11.6.1 Where:

$Concentration_{Calculated}$ = Concentration calculated from result

$Concentration_{Expected}$ = Theoretical concentration of the standard

11.7 Extract Concentration:

The extract concentration is calculated relative to the calibration curve by the instrument software.

11.8 Percent Recovery:

11.8.1 *LCS/LCSD*:

$$\%\text{Recovery} = \frac{\text{Conc}_{\text{spiked}}}{\text{Conc}_{\text{expected}}} * 100$$

11.8.1.1 Where:

$\text{Conc}_{\text{spiked}}$ = Concentration found in the spiked sample

$\text{Conc}_{\text{expected}}$ = Expected concentration

11.8.2 *MS/MSD*:

$$\%\text{Recovery} = \frac{\text{Conc}_{\text{spiked}} - \text{Conc}_{\text{unspiked}}}{\text{Conc}_{\text{expected}}} * 100$$

11.8.2.1 Where:

$\mathbf{Conc_{spiked}}$ = Concentration found in the spiked sample

$\mathbf{Conc_{unspiked}}$ = Concentration found in unspiked sample

$\mathbf{Conc_{expected}}$ = Expected concentration

11.9 Calculation of Dilution Factors

C x D = F

11.9.1 Where:

C = concentration from instrument in ug/kg CN/L

D = dilution factor, if any

F = final concentration in ug/kg CN/L

11.10 $\%\ \text{Solids} = \frac{\text{weight of dried sample}}{\text{weight of wet sample}} \times 100$

11.11 $\text{Final result in CN ug/kg} = \frac{\text{Sample result in CN ug/kg from Lachat}}{\%\ \text{Solids(expressed in decimal form)}} \times 100$

11.12 $\text{Reporting Limit ug/kg} = \frac{1{,}000}{\%\ \text{Solids (expressed in decimal format)}} \times 100$

12 Waste Management

12.1 See GA EPD Laboratory SOP-EPD Laboratory Waste Management Standard Operating procedures, SOP reference 13.8.

13 References

13.1 Method 9012B. Total and Amenable Cyanide (Automated Colormetric, with Off-Line Distillation). SW486. Revision 2, November 2004 9010C/9012B.
13.2 Method 9010C. Total and Amenable Cyanide: Distillation. SW486. Revision 3, November 2004.
13.3 Determination of Cyanide (Macro Distillation Method) in Water, Lachat Application, revised August 2000. QuickChem, Method 10-204-00-1-A.
13.4 EPD Laboratory Quality Assurance Plan, online revision.
13.5 Determination of Cyanide in Waters (Macro Distillation Method). QuickChem Method 10-204-00-1-A. Revision July 22, 2010.
13.6 GA EPD Laboratory SOP's – Initial Demonstration of Capability SOP 6-001, online revision or Continuing Demonstration of Capability SOP 6-002, online revision.
13.7 GA EPD Laboratory SOP-EPD Laboratory Procedures for Control Charts and Control Limits SOP, SOP 6-025, online revision.
13.8 GA EPD Laboratory SOP-EPD Laboratory Waste Management SOP, SOP 6-015, online revision.
13.9 GA EPD Laboratory SOP – Determination of Method Detection Limit, Method Detection Limit SOP 6-007, online revision.
13.10 GA EPD Laboratory Safety Plan – EPD Laboratory Safety / Chemical Hygiene Plan & Fire Safety Plan, online revision.

14 Reporting Limits (RLs), Precision and Accuracy Criteria, and Quality Control Approach

Table 14.1 RLs for EPA SW846 Method 9010C/9012B

Parameter/Method	Analyte	Matrix (aqueous)	
		RL	Unit
EPA SW846 Method 9010C/9012B	Total Cyanide	1000	ug/kg(dry)

Table 14.2 Acceptance Criteria for EPA SW846 Method 9010C/9012B

Method	Analyte	LCS, LCSD, MS, MSD Accuracy Water (%R)	LCSD, MSD Precision Water (RPD)
EPA SW846 Method 9010C/9012B	Total Cyanide in Waste and Sediment	85-115	30
All control limits are static by EPD Lab Default. Control charts are generated twice annually for trend monitoring			

Table 14.3 Summary of Calibration and QC Procedures for Method EPA SW846 9010C/9012B

Method	Applicable Parameter	QC Check	Minimum Frequency	Acceptance criteria	Corrective Action	Flagging Criteria
EPA SW846 Method 9010C/9012B	Total Cyanide in waste and sediment	Initial calibration for all analytes	Initial calibration prior to sample analysis.	Correlation coefficient $\geq$ 0.995 linear regression	Correct problem then repeat initial calibration	
		Second source calibration verification (ICV)	Once per initial calibration	Cyanide concentration within 10% of expected value	Correct problem then repeat initial calibration	
		Initial Demonstration: Demonstrate ability to generate acceptable accuracy and precision using four analysis of a QC check sample, a method blank and a blind sample. In addition, the analyst must prepare one standard.	Once per analyst	QC Acceptance Criteria SOP 3-039 Appendix A and Initial Demonstration SOP (Reference 13.6)	Recalculate results: locate and fix problem with system and then rerun demonstration for those analytes that did not meet criteria	
		Continuing Demonstration: Demonstrate ability to generate acceptable accuracy and precision using a variety of analysis options of a QC sample(s)	Every 6 months	QC Acceptance Criteria SOP 3-039 Appendix A and Continuing Demonstration of Capability SOP(Reference 13.6)		
		Method Blank (MBLK) Distilled	One per batch	Total Cyanide value must be < RL	Correct problem then analyze method blank and all samples processed with the contaminated blank	If unable to re-analyze, flag with a "B"

Table 14.3 Summary of Calibration and QC Procedures for Method EPA SW846 9010C/9012B

Method	Applicable Parameter	QC Check	Minimum Frequency	Acceptance criteria	Corrective Action	Flagging Criteria
EPA SW846 Method 9010C/9012B	Total Cyanide in waste and sediment	Laboratory Control Sample (LCS/ LCSD)	One LCS/LCSD per analytical batch	QC Acceptance Criteria Table SOP 3-039 Appendix A	Correct problem then re-analyze the LCS/LCSD and all samples in the affected batch	If unable to re-analyze, flag with a "J"
		MDL study	Every six months or after major maintenance of the instrument	All Spiked MDLs must have a value greater than 0. Minimum Detection Limits established shall be < the RLs in Table 14.1	Re-do MDL Study	
		MDL analysis	Once per batch or as needed to acquire data points per SOP 6-007, online revision	All Spiked MDLs must have a value greater than 0. All other QC in the MDL blank and MDL sample (i.e., Surrogate Spike or Internal Standard, etc. if included) must meet established criteria	Correct problem and re-run the MDL sample or MDL blank once and initiate a corrective action. If the re-run fails a second time, do not use MDL data. Update corrective action, and use associated sample data	
		Initial Calibration Blank (ICB) *Not distilled	Once per initial calibration	Total Cyanide value must be < RL	Evaluate source of contamination and remove or recalibrate.	
		Matrix Spike (MS/MSD)	10% of samples	QC Acceptance Criteria Table SOP 3-039 Appendix A	Evaluate out of control event, reanalyze or flag data	
		Continuing Calibration Check (CCC)	Prior to sample analysis, after every 10 samples and at the end of sample run.	Cyanide concentration within 10% of expected value	Correct problem then reanalyze CCC and all samples in affected batch	
		Continuing Calibration Blank (CCB)	After every 10 samples and at the end of sample run.	Cyanide concentration < RL	Correct problem then reanalyze CCB and all samples in affected batch	
		Low level distilled standard (1000 ug/kg)	Once per analytical run.	CN value must be ± 50% of expected value	Evaluate recovery exceedances, reanalyze or recalibrate.	
		High level distilled standard (20000 ug/kg)	Once per analytical run	CN value must be ± 10% of expected value	Evaluate recovery exceedances, reanalyze or recalibrate.	

Table 14.3 Summary of Calibration and QC Procedures for Method EPA SW846 9010C/9012B

Method	Applicable Parameter	QC Check	Minimum Frequency	Acceptance criteria	Corrective Action	Flagging Criteria
EPA SW846 Method 9010C/9012B	Total Cyanide in waste and sediment	MDL Low level Spike (MDLS) 1000 ug/kg	Once per analytical batch	All batch QC must be valid	Correct problem then reanalyze the affected batch	
		MDL Blank (MDLB)	Once per analytical batch	All batch QC must be valid	Correct problem then reanalyze the affected batch	

Appendix A, Table A.1 – Quality Assurance Criteria for EPA SW846 Method 9010C/9012B

Table A.1 Quality Assurance Criteria for EPA SW846 Method 9010C/9012B

QC Type	Analyte	Accuracy(%R) LCL		UCL	Precision (%RPD)
LCS/LCSD	Total Cyanide In Waste in Sediment	85	-	115	30
MS/MSD	Total Cyanide In Waste in Sediment	85	-	115	30

***All hazardous waste project limits are static by EPD Lab Default.**
Control Chart data generated from 01/01/2018- 01/01/2021

Updates to Previous Version:
Updated for online revision. Appendix A added.
Section 2
Section 9
Section 10
Table A.1
Table 14.3