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EPA Method 335.4 - Determination of Total Cyanide by Semi-Automated Colorimetry

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1 Scope and Application

1.1 This method is applicable to the determination of cyanide in drinking, ground, surface and saline waters, domestic and industrial wastes. The cyanide as hydrocyanic acid (HCN), is released from cyanide complexes by means of distillation. Cyanides are converted to cyanogen chloride by reactions with chloramine-T, which subsequently reacts with pyridine and barbituric acid to give a reddish-violet colored complex which is measured colorimetrically at 570 nm. The method is modified to use the MIDI-VAP midi-cyanide distillation system and the Lachat Quickchem Auto-Analyzer. Method 10-204-00-1-A.

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 13.3) 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.

2.6 Calibration Blank (CB), Initial Calibration Verification Blank (ICB), Method Blank (MBLK), Method Detection Limit Blank (MDLB) 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.

3 Interferences

3.1 Several interferences are encountered with this method. Some of the known interferences are aldehydes, nitrate-nitrite, oxidizing agents, such as chlorine, thiocyanate, thiosulfate and sulfide. Multiple interferences may require the analysis of a series of laboratory fortified sample matrices (LFM) to verify the suitability of the chosen treatment. Some interferences are eliminated or reduced by the distillation.

3.2 Sulfides adversely affect the procedure by producing hydrogen sulfide during distillation. If a drop of the sample on lead acetate test paper indicates the presence of sulfide (paper darkens when sulfide is present), treat 25 ml more of the stabilized sample (pH ≥12) than that required for the cyanide determination with powdered cadmium carbonate. Yellow cadmium sulfide precipitates if the sample contains sulfide. Repeat this operation until a drop of the treated sample solution does not darken the lead acetate test paper. Filter the solution through a dry filter paper into a dry beaker, and from the filtrate, measure the sample to be used for analysis. Reconstitute the particulate that is filtered with the sample prior to distillation. Avoid a large excess of cadmium and a long contact time in order to minimize a loss by complexation or occlusion of cyanide on the precipitated material.

3.3 High results may be obtained for samples that contain nitrate and/or nitrite. During the distillation nitrate and nitrite will form nitrous acid that will react with some organic compounds to form oximes will decompose under test conditions to generate HCN. The interference of nitrate and nitrite is eliminated by pretreatment with sulfamic acid. See 10.1.15 for procedure.

3.4 Method interferences may be caused by contaminants in the reagent water, reagents, glassware, and other sample processing apparatus that bias analyte response.

3.5 Other compatible procedures for the removal or suppression of interferences may be employed provided they do not adversely affect the overall performance of the method.

3.6 Oxidizing agents, such as chlorine, decompose most of the cyanides. Test a drop of the sample with potassium iodide-starch paper (KI-starch paper) at time of collection; a blue color indicates the need for treatment. Add ascorbic acid, a few crystals at a time, until a drop of sample produces no

color on the indicator paper; then add an additional 0.06g of ascorbic acid for each liter of sample volume. Sodium arsenite has also been employed to remove oxidizing agents.

4 Safety

4.1 Refer to the EPD Laboratory Safety / Chemical Hygiene Plan & Fire Safety Plan, online revision. Reference 13.9.

5 Apparatus and Equipment

5.1 Sample Container: 250 ml Nalgene bottle

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
5.14.2 Expiration date one year from date of receipt if no expiration date given.
5.15 Lead Acetate Test 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
5.16.2 Expiration date one year from date of receipt if no expiration date given.
5.17 Narrow range pH Test Strips - Fisherbrand pH Paper 10.0-12.0 Cat. No. 13-640-513 or equivalent.

6 Reagents

6.1 Reagent Water:
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 mg/L CN standard/CCB/ICB/MBLK):
Dissolve 10g NaOH in reagent water and bring to volume in a IL volumetric flask, or dissolve 40g of 50% NaOH in reagent water and bring to volume in a 2L volumetric flask. Prepare several liters as one batch to be used for carrier and standards. Prepare every two weeks.

6.3 Magnesium Chloride reagent, 51 % w/v):
Dissolve 51g $MgCl_26H_2O$ in reagent water and dilute to 100ml. Reagent is stable for 3 months.
6.3.1 Reagent has been modified from EPA method per Lachat methodology.
6.4 Sulfuric Acid, 18N:
Slowly add 50ml of ACS grade concentrated H_2SO_4 to 50 ml of reagent water. Reagent is stable for 3 months.
6.5 Lead Acetate Paper: sulfide indicator paper (see 5.15)
6.6 Starch Iodide Paper: oxidant indicator paper (see 5.16)
6.7 Nitrate test strips: (see 5.14)
6.8 Chloramine-T:
Dissolve 2g of ACS grade chloramine-T hydrate to 500ml of DI 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:
In the fume hood, place 15g of ACS grade barbituric acid 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 ACS grade pyridine while stirring and mix until the barbituric acid dissolves. Add 15ml 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 (pH 5.2+/- 0.2):

Add 97g of ACS grade Potassium Phosphate Monobasic, anhydrous, (KH_2PO_4) in a 1L volumetric flask and dilute to volume with DI water. Prepare fresh monthly.

6.10.1 Reagent has been modified from EPA method per Lachat methodology.

6.11 Ascorbic Acid: Crystal:
If oxidizing agents are present.

6.12 Sulfamic Acid: (CASRN-212-57-3)
If nitrate/nitrite concentration is ≥5.0 mg/L.

6.13 Cadmium Carbonate
If sulfide is present.

6.14 Cyanide Stock Standard A, 1000mg CN/L:
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.

6.15 Cyanide Stock Standard B, 10mg CN/L:
Pipette 10ml Cyanide Stock Standard A in a 1L volumetric flask. Dilute to mark with 0.25N NaOH and mix. Standard is good for 14 days.

6.16 Calibration Standards:
7 levels of calibration standards are prepared by the addition of aliquots of Cyanide Stock Standard B, 10mg CN/L to Carrier, 0.25N Sodium Hydroxide Solution (see 6.2) using as follows:

Table 6.16.1 – Working Cyanide Standards

Cyanide Stock B (10 mg/L) (mL)	Final Volume Carrier (.25M NaOH) (mL)	Cyanide Concentration (CN) (mg/L)	Cyanide Concentration (CNTAL) (ug/L)
NA	100 mL	0.00	0
2 ml	1 L	0.02	20
1 ml	200 ml	0.05	50
2 ml	200 ml	0.10	100
4 ml	200 ml	0.20	200
6 ml	200 ml	0.30	300
8 ml	200 ml	0.40	400
10 ml	200 ml	0.50	500

6.16.2 Standards are stable for 14 days.

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

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

6.17.2 The ICV stock standard is used as a second source standard.

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

6.17.4 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.

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

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

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

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

6.19.2 The ICV solution is stable for 14 days.

6.20 1N NaOH solution:
Dissolve 20g NaOH in reagent water and bring to volume in a 500 ml volumetric flask. Prepare fresh every 6 months.

7 Sample Collection

7.1 Samples are collected in 250 ml amber plastic bottles.

7.1.1 For WQ, WPCP and Hazardous Water projects, NAOH pellets are added to the bottles in the receiving lab, prior to collection in the field by sample collectors.

7.1.2 See Appendix B for Drinking Water Cyanide Program sample collection instructions.

7.1.2.1 These samples are monitored every 10 years and are collected by drinking water customers, not EPD field collectors.

7.1.2.2 The drinking water cyanide samples containers contain 1.0 gram of sulfamic acid.

7.1.2.3 Once the sample bottle is filled with sample and mixed, 0.1 grams of ascorbic acid is then added. The sample is inverted and mixed again.

7.1.2.4 Finally, 7 NaOH pellets are added to the sample as a preservative. The sample is inverted and mixed one last time.

7.2 Samples are preserved to a pH of $\geq$ 12.

7.3 Sample preservation is checked in the receiving lab at time of receipt.

7.3.1 Sample pH is checked with disposable transfer pipets (see 5.12). A clean disposable pipet is used to draw up a few drops of the sample. The drops are then placed on appropriate narrow range pH paper.

7.3.2 Never dip the test strip into the sample.

7.3.3 If the sample pH is not $\geq$ 12, the collector is notified. The sample is then preserved in the receiving lab and a comment is placed on the test code that the sample was preserved in the laboratory. The result is “J” flagged as estimated due to sample not preserved at time of collection.

7.4 Samples are stored at 0 - 6º C (not frozen).

7.5 Sample holding time is 14 days.

8 Calibration

8.1 Calibration Standards:

8.1.1 The calibration curve consists of calibration standards and concentrations listed in Table 6.16.1.

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 $r \geq 0.995$ or $r^2 \geq 0.990$ using a linear regression. Dilute all samples with a response greater than the high standard.

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 (0.02 mg/L or 20 ug/L) 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 (0.40 mg/L or 400 ug/L) 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 0.02 mg /L or 20 ug/L must be analyzed with each batch to perform an ongoing MDL study. All batch QC must be valid to report this result.

8.6.1 The MDLS must be poured into a 250 ml sample collection bottle before distillation. Record lot # of sample bottle 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 MDLB must be poured into a 250 ml sample collection bottle before distillation. Record lot # of sample bottle used.

9 Quality Control

9.1 Refer to Table 14.1 for Reporting Limits (RL's), Appendix A, Table A.1 and A.2 for Quality Control Acceptance Criteria, and Table 14.2 for Quality Control Procedures associated with this method.

9.2 See reference 13.6 for control charting procedures.

9.3 See reference 13.5 for training certification procedures.

9.3.1 For Initial Demonstrations of Capability (IDC), Method 335.4 requires a recovery range of 90% - 110% for CN and 85%-115% for CNTAL (see calculation 11.8).

9.3.1.1 The EPD Laboratory sets a 20% 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 20% RSD is required (see calculation 11.4).

9.4 Control Limits:

9.4.1 Method 335.4 requires LCS/LCSD control limits to be adjusted through the use of control charts.

9.4.2 Default control limits for recovery for LCS/LCSD pairs are based on Section 9.3.3 of EPA Method 335.4(reference 13.1) as noted in Table 9.4.8.1 below. The default limits are 90% - 110% recovery for CN and CNTAL.

9.4.3 LCS/LCSD recovery limits are adjusted through the use of control charts for drinking water, WPCP and water quality samples only (CN test code).

9.4.4 The EPD Laboratory sets default LCS/LCSD precision control limits to 0 – 20% RPD for drinking water, WQ and WPCP (CN test code) and Hazardous Waste project batches (CNTAL test code).

9.4.5 EPA Method 335.4 requires recovery control limits of 90 -110% for matrix spikes therefore the MS/MSD recovery limits are static for drinking water, WQ and WPCP (CN test code) and Hazardous Waste project batches (CNTAL test code). The EPD Laboratory applies MS recovery limits to MSDs. Control limits for recovery for MS/MSD pairs are based on Section 9.4.2 of EPA Method 335.4.

9.4.6 By default, the EPD Laboratory sets default MS/MSD precision control limits to be 0-20% RPD for drinking water, WQ and WPCP samples. MS/MSD precision limits are static.

9.4.6.1 Hazardous Waste Project batches (test code CNTAL) will have default and static precision control limits for MS/MSD of 0-30% RPD.

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

9.4.8 See Administrative SOP for Control Charting and Control Limits, reference 13.6 for further details.

Table 9.4.8.1 – Default Quality Assurance Criteria for Method EPA 335.4 – Drinking Water, WPCP and Water Quality Samples(CN)

QC Type	Analyte	Accuracy(%R) LCL	Accuracy(%R) UCL	Precision (%RPD)
LCS/LCSD	Total Cyanide(CN)	90	110	20
MS/MSD	Total Cyanide(CN)	90	110*	20*

*MS/MSD control limits are static by EPD Lab default. Control charts are processed for monitoring purposes only.

Note: The default control limits are presented to assist in defining control limits established with control charts and are not used as batch acceptance criteria.

Table 9.4.8.2. – Default Quality Assurance Criteria for Method EPA 335.4* – Hazardous Waste Project Water Samples(CNTAL)

QC Type	Analyte	Accuracy(%R) LCL	UCL	Precision (%RPD)
LCS/LCSD	Total Cyanide (CNTAL)	90 - 110		20
MS/MSD	Total Cyanide (CNTAL)	90 - 110		30
***All hazardous waste project limits are static by EPD Lab Default.**				

9.5 Batching:

9.5.1 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.

9.5.2 For batches of 10 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.

9.5.3 Each batch must have an LCS, LCSD and a Method Blank.

9.6 MDL Studies:

9.6.1 MDL studies must be performed every 6 months (twice annually). See reference 13.8 for further details.

10 **Procedure**

10.1 Procedure for Distillation

10.1.1 Remove sample bottles, 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 pipettors 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 Check pH of sample to make sure it is ≥ 12 using pH test strips (See Section 5.17).

10.1.3.1 If pH is <12, add 3 NaOH pellets in sample bottle. Mix well. Recheck pH. Continue to add NaOH pellets until pH is ≥ 12. A corrective action must be completed, and sample result will be "J" flagged as estimated due to sample received outside of required pH range.

10.1.4 Check for sulfide presence with lead acetate test paper. Refer to section 3.2 if sulfide is present.

10.1.4.1 If a drop of the sample on lead acetate test paper indicates the presence of sulfide (paper darkens when sulfide is present), treat 25 ml more of the stabilized sample (pH ≥12) than that required for the cyanide determination with powdered cadmium carbonate. Repeat this operation until a drop of the treated sample solution does not darken the lead acetate test paper

10.1.4.2 Yellow cadmium sulfide precipitates if the sample contains sulfide.

10.1.4.3 Filter the solution through a dry filter paper into a dry beaker, and from the filtrate, measure the sample to be used for analysis.

10.1.4.4 Reconstitute the particulate that is filtered with the sample prior to distillation. Avoid a large excess of cadmium and a long contact time in order to minimize a loss by complexation or occlusion of cyanide on the precipitated material.

10.1.5 Check for oxidant presence with starch iodide indicator paper.

10.1.5.1 If there is a presence of oxidants, add a few crystals of ascorbic acid at a time until a drop of sample produces no color on the indicator paper. Then add an additional 0.6 grams of ascorbic acid for each liter of sample volume.

10.1.6 Check for presence of nitrate/nitrite using Nitrate/Nitrite test strips. Refer to 5.14.

10.1.6.1 If there is a presence of nitrate and or nitrite of 5.0 mg/L or greater, see 10.1.15 for procedure.

10.1.7 For **drinking water program cyanide samples only**, the MBLK and the LCS/LCSD must include 0.1 grams of ascorbic acid and 1.0 grams of sulfamic acid to show that no matrix interference exists due to the preservatives sulfamic acid and ascorbic acid. It is preferred that the same lot # of ascorbic acid that is used for the samples is also used for the MBLK, the low-level standard (0.02 mg/L), the high-level standard (0.40 mg/L), and the LCS/LCSD. Refer to SOP 3-010 Appendix B.

10.1.8 For samples, add 2 or 3 boiling chips to the back-reflux flask. Then pour 50 ml of the sample into the flask.

10.1.9 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 0.300 mg/L (300 ug/L) directly to the boiling chips (See Section 11.3 for calculation). Finally add 50 ml of 0.25N NaOH that was stored in a 250 ml sample collection bottle to the flask. 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 bottle used.

10.1.10 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 0.300 mg/L (300 ug/L) directly to the boiling chips (See Section 11.3 for calculation). Finally add 50 ml of the sample to the flask.

10.1.11 Add 50 ml of 0.25N NaOH to the front absorber flasks.

10.1.12 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.

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

10.1.14 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.

10.1.15 If there is a presence of nitrate and or nitrite of 5.0 mg/L or greater, slowly add 0.2g of Sulfamic acid through the air inlet tube of the sample, the MBLK, the low level standard (0.02 mg/L), the high level standard (0.40 mg/L) and the LCS/LCD. Let mix for 3 minutes prior to the addition of H_2SO_4.

10.1.16 Slowly pipette 5 ml of 18 N Sulfuric Acid through the air inlet tube. Rinse tube with DI water and let mix for 3 minutes.

10.1.17 Pipette 2.0 ml of magnesium chloride reagent through the air inlet tube. Rinse tube with DI water and let mix for 3 minutes.

10.1.18 Make sure to measure the temperature of the distillation system by placing a certified thermometer probe into a distillation tube containing sand. 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. The optimal temperature is 126 ± 10ºC.

10.1.19 Switch on power to the distillation system and set timer to 105 minutes. Temperature is set at 126ºC and will permit rapid boiling.

10.1.20 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.

10.1.21 Record start and end time of digestion on Digestion Log Sheet.

10.1.22 Reflux for at least 1 hour. Timer will switch off heaters, 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.

10.2 Procedure for Analyzing Samples using the Lachat

10.2.1 Turn on the computer, instrument, autosampler and pump.

10.2.2 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.

10.2.3 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.

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

10.2.5 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.

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

10.2.7 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 is placed in the run log.

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

10.2.9 Load your standards in the standard rack, putting your highest standard in the first position. Then load samples in the sample tray.

10.2.10 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.

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

10.2.12 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.

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

10.2.14 Re-digest all samples (at a dilution) for which the responses are greater than the high standard.

10.2.15 To prepare dilutions, use Carrier, 0.25N Sodium Hydroxide Solution (see 6.2).

10.2.16 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.

10.3 Shutdown Procedure

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

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

10.3.3 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.

10.3.4 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.

10.3.5 Make sure not to dispose of Cyanide waste in the sink. It needs to be kept in properly labeled 5 gallon containers. When full, the containers need to be placed in the chemical storage building and the receiving lab supervisor needs to be notified.

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

11 Calculations

11.1 The weighted external standard calibration is calculated by the instrument software and is documented in the instrument software.

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:**
$\text{Conc}_{\text{spiked}}$ = Concentration found in the spiked sample
$\text{Conc}_{\text{unspiked}}$ = Concentration found in unspiked sample
$\text{Conc}_{\text{expected}}$ = Expected concentration

11.9 Calculation of Dilution Factors

C x D = F

11.9.1 Where:
C = concentration from instrument in ug/L CN or mg/L CN
D = dilution factor, if any
F = final concentration in ug/l CN or mg/L CN

12 Waste Management

12.1 See GA EPD Laboratory SOP-EPD Laboratory Waste Management Standard Operating procedures, SOP reference 13.7.

13 References

13.1 EPA Method 335.4, Determination of Total Cyanide by Semi-Automated Colorimetry, Rev. 1.0, August 1993.

13.2 Manual for the Certification of Laboratories Analyzing Drinking Water, EPA/815-R-05-004, January 2005.
13.3 EPD Laboratory Quality Assurance Plan, online revision.
13.4 Determination of Cyanide in Waters (Macro Distillation Method). QuickChem Method 10-204-00-1-A. Revision July 22, 2010.
13.5 GA EPD Laboratory SOP's – Initial Demonstration of Capability SOP 6-001, online revision or Continuing Demonstration of Capability SOP 6-002, online revision.
13.6 GA EPD Laboratory SOP-EPD Laboratory Procedures for Control Charts and Control Limits SOP, SOP 6-025, online revision.
13.7 GA EPD Laboratory SOP-EPD Laboratory Waste Management SOP, SOP 6-015, online revision.
13.8 GA EPD Laboratory SOP – Determination of Method Detection Limit, Method Detection Limit SOP 6-007, online revision.
13.9 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 335.4

Parameter/Method	Analyte	Matrix (aqueous)	
		RL	Unit
EPA 335.4	Total Cyanide (CN)	0.020	mg/L
EPA 335.4	Total Cyanide (CNTAL)	20	20 ug/L

Table 14.2 Summary of Calibration and QC Procedures for Method EPA 335.4

Method	Applicable Parameter	QC Check	Minimum Frequency	Acceptance criteria	Corrective Action	Flagging Criteria
EPA 335.4	Total Cyanide	Initial calibration for all analytes	Initial calibration prior to sample analysis.	Correlation coefficient ≥ 0.995 linear regression	Correct problem then repeat initial calibration	
		Second source calibration verification (ICV)	Once per initial calibration or quarterly, whichever is sooner.	Cyanide concentration within 10% of expected value	Correct problem then repeat initial calibration	

Table 14.2 Summary of Calibration and QC Procedures for Method EPA 335.4

Method	Applicable Parameter	QC Check	Minimum Frequency	Acceptance criteria	Corrective Action	Flagging Criteria
EPA 335.4	Total Cyanide	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 3-010 Appendix A and Initial Demonstration SOP (Reference 13.5)	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 3-010 Appendix A and Continuing Demonstration of Capability SOP(Reference 13.5)		
		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"
		Laboratory Control Sample (LCS/ LCSD)	One LCS/LCSD per analytical batch	QC Acceptance Criteria Table SOP 3-010 Appendix A	Correct problem then reanalyze the LCS/LCSD and all samples in the affected batch	If unable to re-analyze, flag with a "J"
		MDL Study	Twice per year	Detection limits established shall be < the RL's in Table 14.1	None	
		Initial calibration blank (ICB) Not distilled	Once per initial calibration	Total Cyanide value must be < RL.	Correct problem then repeat initial calibration	
		Matrix Spike (MS/MSD)	10% of samples.	QC Acceptance Criteria Table SOP 3-010 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) Not distilled	After every 10 samples and at the end of sample run.	Cyanide concentration must be below reporting limit.	Correct problem then reanalyze CCB and all samples in affected batch	
		Low level distilled standard(0.02 mg/L or 20 ug/L)	Once per analytical run.	CN value must be ± 50% of expected value	Evaluate recovery exceedances, reanalyze or recalibrate.	

Table 14.2 Summary of Calibration and QC Procedures for Method EPA 335.4

Method	Applicable Parameter	QC Check	Minimum Frequency	Acceptance criteria	Corrective Action	Flagging Criteria
EPA 335.4	Total Cyanide	High level distilled standard(0.40 mg/L or 400 ug/L)	Once per analytical run	CN value must be ± 10% of expected value	Evaluate recovery exceedances, reanalyze or recalibrate.	
		MDL Low level Spike (MDLS) 0.02 mg/L or 20 ug/L	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 Method 335.4- Determination of Total Cyanide by Semi-Automated Colorimetry

Table A.1 – Current Control Limits – EPA 335.4
Drinking Water, WPCP and Water Quality Samples

QC Type	Analyte	Accuracy (%R) LCL		UCL	Precision (%RPD)
LCS/LCSD	Total Cyanide (CN)	90	-	110	15
MS/MSD	Total Cyanide (CN)	90*	-	*110	20

***MS/MSD Control limits are static by EPA Method/EPD Lab default.**
***Control chart data generated from 01/01/2018 – 01/01/2020**

Table A.2 – Current Control Limits – EPA 335.4
Hazardous Waste Project Samples

QC Type	Analyte	Accuracy (%R) LCL		UCL	Precision (%RPD)
LCS/LCSD	Total Cyanide (CNTAL)	90	-	110	20
MS/MSD	Total Cyanide (CNTAL)	90	-	110	30

***Control limits static by EPD Lab default.**
***Control charts are generated twice annually for informational purposes only.**
*** Control chart data generated from 01/01/2017 – 01/01/2020**

Updates to Previous Version:
Updated for online revision. Appendix A added.