State of Connecticut

Department of Energy and Environmental Protection

Recommended Reasonable Confidence Protocols

Quality Assurance and Quality Control Requirements

Determination of Total Cyanide By SW-846 Methods 9010/9012/9014

Version ~~2~~3.0

Month 2023

Written by the Connecticut ~~DEP~~DEEP QA/QC Workgroup

Revision	Comments	Date
1.0	First Version for publication	7/2005
2.0	Final version based upon public comments	July 2006
3.0	Updates to reflect CAM method updates to improve consistency between different states.	Month 2023

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Table of Contents

Table of Tables

Preliminary Draft for DEEP Laboratory QA/QC Workgroup Review and Comment Only – Not to be used or relied on for any other purpose, may be subject to significant editing and revision.

ACRONYNM LIST

ACRONYM	DEFINITION
CASN	Chemical Abstracts Service Number
CCB	Continuing calibration blank
CCV	Continuing calibration verification
CN	Cyanide
CN^-	Cyanide ion (free Cyanide)
CNCl	Cyanogen chloride
%D	Percent difference
DEEP	CT Department of Energy and Environmental Protection
EP	Environmental Professional
g	Grams
HCl	Hydrochloric acid
HCN	Hydrocyanic acid
HNO_3	Nitric acid
ICB	Initial calibration blank
ICV	Initial calibration verification
LCS/LCSD	Laboratory control sample / Laboratory control sample duplicate
LLOQ	Lower limit of quantitation
MB	Method blank
MD	Matrix duplicate
mg/L	Milligram per liter
mg/kg	Milligram per kilogram
mL	Milliliter
MS	Matrix spike
NaOH	Sodium hydroxide
nm	Nanometer
%R	Percent recovery
r/r^2	Correlation coefficient
RL	Reporting limit
RPD	Relative percent difference
RSR/RSRs	Remediation Standard Regulations
QA	Quality assurance
QC	Quality control
µg/L	Microgram per liter
µm	Micrometer

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1.0 Quality Assurance and Quality Controls Requirements for SW-846 Methods 9010/9012/9014

1.1 Method Overview

Method 9010 is a distillation procedure for cyanide~~.~~ ("CN"). The distillation procedure breaks down most metallo-cyanide complexes and removes the ~~cyanide~~CN from most potential interferences. After distillation the ~~cyanide~~CN may be determined using the manual colorimetric or titration procedure found in Method 9014. Method 9012 utilizes an automated colorimetric procedure and is considered equivalent to ~~the colorimetric procedure in~~ Method 9014 and may also be used.

All method references are to the latest promulgated version of the method found in Test Methods for Evaluating Solid Waste, SW-846.

1.2 Summary of SW-846 Methods 9010/9012/9014

Total Cyanide includes Free Cyanide ("CN^-") plus nitriles (organic cyanides), other simple cyanides such as cyanide salts, and stable metallo-cyanide complexes including iron-cyanides. Total Cyanide is defined as the sum of cyanides, as hydrocyanic acid ("HCN"), released during the aggressive catalytic, mineral acid reflux distillation procedure described in SW-846 Method 9010.

~~1.2.1~~ Prior to analysis, the liquid samples must be distilled according to Method 9010. The midi-distillation procedure may also be used as it is considered equivalent.

The following determinative methods may be used for analysis of Total Cyanide in solution/distillates are listed in Table 1.0:

Table 1.0: Determinative Methods for Total Cyanide Analysis

Method	Title Description
SW-846 9014	Manual colorimetric UV spectrometry for the determination of free (non-complexed) CN^- and HCN in solution/distillates.[1]
SW-846 9012	Automated colorimetric UV spectrometry for the determination of free CN^- and HCN in solution/distillates
Standard Method 4500-CN	Includes colorimetric (equivalent to SW-846 Method 9014), titrimetric, and potentiometric procedures for the determination of HCN in distillates
[1]This method also includes titrimetric determination; however, the sensitivity of the titrimetric method may not meet data quality objectives.	

~~1.2.2~~ In the colorimetric measurement, the ~~cyanide~~CN is converted to cyanogen chloride ("CNCl") by reaction of ~~cyanide~~CN with chloramine-T at a pH less than 8. After the reaction is complete, color is formed upon the addition of pyridine-barbituric acid reagent. The absorbance is read at 578 nm for the complex formed with pyridine-barbituric acid reagent and CNCl. ~~To obtain colors of comparable intensity, it is essential to have the same salt content in both the sample and the standards.~~ For the colorimetric method of analysis (SW-846 9014 and Standard Method 4500-CN^-), it is important to have the same reagent concentrations in both the sample

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and the standards to obtain colors of comparable intensity. The colorimetric procedure is used for cyanide concentrations below 1 mg/L and is sensitive to about 0.02 mg/L.

~~1.2.3~~ The titration measurement uses a standard solution of silver nitrate to titrate ~~cyanide~~ CN in the presence of a silver sensitive indicator. The titration procedure using silver nitrate with p-dimethylamino-benzal-rhodanine indicator is used for measuring concentrations of ~~cyanide~~CN exceeding 0.1 mg/L ~~(0.025 mg/250 mL of absorbing liquid).~~. The titration procedure is generally not suitable for aqueous samples due to its high ~~detection~~reporting limit~~.~~ ("RL"), or lower limit of quantitation ("LLOQ").

~~1.4~~1.3 Method Interferences

Refer to SW-846 Method 9010 and Standard Method 4500-CN^- for further information on method interferences. Many potential interferences are eliminated in the acidic reflux-distillation procedure used for Total CN (SW-846 Method 9010 and Standard Method 4500-CN^-). Several common interferences and corrective measures are summarized as follows.

1.3.1 Chemical Interferences

~~1.4.1~~ Interferences are eliminated or reduced by using the distillation procedure. Chlorine and sulfide are interferences in SW-846 Method 9010.

~~1.4.2~~ Oxidizing agents, such as chlorine, decompose most ~~cyanides.~~CN compounds and complexes. Chlorine interferences can be removed by adding an excess of sodium arsenite, sodium thiosulfate, or ~~other agent~~ascorbic acid (see Table ~~2A)~~5.0 to ~~the sample~~aqueous samples prior to preservation with base to reduce the chlorine ~~to~~(Cl_2) to non-interfering chloride ~~which does not interfere.~~(Cl^-).

~~1.4.3~~ 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.

~~1.4.4 High~~Positive interferences for CN (high bias 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 hydrocyanic acid (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.

~~1.4.5~~ Thiocyanate is reported to be an interference when present at very high levels. Levels of 10 mg/L were not found to interfere.

~~1.4.6~~ Fatty acids, detergents, surfactants, and other compounds may cause foaming during the distillation when they are present in high concentrations and may make the endpoint for the titrimetric determination difficult to detect. Refer to ~~Sec. 6.7 of Method 9010C~~SW-846 Methods 9010 and 9012 for an extraction procedure to eliminate this interference.

1.3.2 Physical Interferences

Samples containing solids of an amount and/or size as to interfere with agitation and homogenization of the sample mixture in the distillation flask, or so much oil or grease as to interfere with the formation of a homogeneous emulsion may be extracted with water (and hexane if heavy grease is present) at pH 10 or

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greater to minimize this potential interference as described in SW-846 Method 9013, Cyanide Extraction Procedure for Solids and Oils.

1.3.3 Cross Contamination

Analysis of blanks provides information about the presence of contaminants. When potential interferences or high levels of target compounds are detected in blanks, the laboratory should try and find the source of the contamination and eliminate it. **Subtracting blank concentrations from sample results is not permitted.** Any method blank exceedances should be fully documented in the laboratory report narrative.

1.~~5 General~~4 Quality Control Requirements for SW-846 Methods 9010/9012/9014

~~1.3~~1.4.1 Reporting Limits/Lower Limits of Quantitation for SW-846 Methods 9010/9012/9014

The RL/LLOQ for an individual analyte is dependent on the concentration of the lowest non-zero standard in the initial calibration or the low-level calibration verification ("LLCV"), analyzed under identical conditions as the sample, with adjustments made for the sample size, preparation factors, percent solids, dilution factors, ~~sample weight or volume, moisture content (for soils/sediments), and any dilutions~~ etc., as required.

The RL/LLOQ for the titration is based upon the normality of the silver nitrate, the sample volume titrated, and the sample weight or volume, moisture content (for soils/sediments), and any dilutions. To utilize the titrimetric procedure for aqueous samples, the CN concentration must be high enough to require 0.20 mL silver nitrate (after blank subtraction). For soil samples, the titrimetric procedure may be used as long as the RL/LLOQ for a 0.20 mL net titration is below the ~~detection limit~~ RL/LLOQ required. Table 2.0 lists approximate RL/LLOQs for various matrices utilizing these methods. Solid matrices in this table assume 100% solids.

Table 2.0: Typical Reporting Limits/ Lower Limits of Quantitation

Matrix	Typical Reporting Limit
Aqueous	0.005 to 0.010 mg/L
Soil and Sediment	1.0 mg/kg

Moisture content of soils and sediments will raise the RL/LLOQ, as all results must be reported on a dry weight basis for these two matrices. Sample dilution or lower sample weight/volume will also cause the RL/LLOQs to be raised. It is the responsibility of the data user, in concert with the laboratory, to establish the range and required RL/LLOQ for the target analyte to meet Remediation Standard Regulations ("RSRs") criteria. To meet the limits, it may be necessary to modify the analytical method to improve sensitivity. In such cases, the modifications must be noted in the laboratory report narrative.

~~Sample preservation, container and analytical holding time specifications for surface water, groundwater, soil, and sediment matrices for trace metals are listed in Table 2A of this document. Moisture content of soils and sediments will raise the RL, as all results must be reported on a dry weight basis for these two matrices. Sample dilution or lower sample weight/volume will also cause the RL's to be raised.~~

~~**1.7 Reporting Limits for Methods 9010/9012/9014**~~

~~The Reporting Limit (RL) for the colorimetric methods is based upon the lowest standard in the initial calibration and taking into account the exact sample mass, any dilution factors, percent moisture, etc.~~

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~~The RL for the titrametric method is based upon the normality of the silver nitrate, the sample volume titrated, and the sample weight/volume taken for distillation.~~

~~1.6~~1.4.2 Quality Control Requirements for SW-846 Methods 9010/9012/9014

This protocol is restricted to use by, or under the supervision of, analysts who are experienced in using distillation preparation methods and colorimetric or titration methods as quantitative tools and are skilled in the correction of spectral, chemical, and physical interferences described in this method.

Refer to SW-846 Chapter One for general quality control ("QC") procedures for all inorganic methods, including SW-846 Methods 9010, 9012, and 9014. These requirements ensure that each laboratory maintain a formal quality assurance ("QA") program and records to document the quality of all inorganic data and be certified by the Connecticut Department of Public Health for the analysis performed. QC procedures necessary to evaluate the instrument's operation can also be found in SW-846 Chapter One, ~~Section 2.0,~~ and the SW-846 Methods 9010/9012/9014 and include evaluation of calibrations and performance of sample analyses.

The minimum requirements for the QA program include ~~initial demonstration~~Initial Demonstration of ~~laboratory proficiency,~~Capability ("IDOC"), ongoing analysis of standards and blanks to confirm acceptable continuing performance, and analysis of laboratory control samples ~~(~~("LCS~~)~~") and/ or matrix spikes ("MS") to assess accuracy and analysis of LCS duplicates ("LCSD") or matrix duplicates ("MD") to assess precision ~~and accuracy. The use of~~ . A site -specific ~~matrix spikes and matrix duplicates is highly~~MS sample is required for solids samples (soil/sediment). However, site-specific MS/MD samples are strongly recommended~~.~~ from each site and for each matrix type sampled. Evaluation of sample matrix effects on ~~mercury~~element recovery is key to making ~~good~~informed decisions. Percent recovery data from site-specific samples allow the environmental professional ("EP") to make informed decisions regarding contamination levels at the site. Batch MS/MSD results do not give any indication of site-specific matrix interferences or analytical problems related to the specific site matrices and are generally discouraged. Field, rinsate, or other blanks should not be used for MS/MSD's. A laboratory may substitute a matrix spike/matrix spike duplicate in lieu of the MS/MD.

~~**1.6.3 Site Specific Matrix Spike (MS) and Matrix Duplicate (MD) Samples**~~

~~It is strongly recommended that site-specific MS/MD samples be analyzed from each site, and each matrix type sampled. Percent recovery data from site-specific samples allow the EP to make informed decisions regarding contamination levels at the site. Batch MS/MD results do not give any indication of site-specific matrix interferences or analytical problems related to the specific site matrices and are in general discouraged.~~

~~Field blanks, rinsate blanks, etc. should not be used for MS/MD's. A laboratory may substitute a matrix spike/matrix spike duplicate in lieu of the MS/MD~~

Laboratories must document and have on file an ~~Initial Demonstration of Proficiency~~IDOC for each combination of sample preparation and determinative method being used. ~~These data must meet or exceed~~An IDOC must be completed and documented when a method is initially started up, whenever a method is substantially modified, or new laboratory staff is trained to perform this method. These data must meet or fall within the performance standards as presented in Section 1.~~5~~4 and Table 1A of this RCP. See ~~Section 4.4.1 of~~ SW-846 Chapter One and SW-846 Method 9010/9012/9014 for the procedure. The ~~Initial Demonstration of Proficiency~~IDOC must include the following elements provided in Table 3.0:

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Table ~~1.1~~3.0: IDOC Requirements

QC Element	Performance Criteria
Initial Calibration	Table 1A
Continuing Calibration	Table 1A
Method Blanks	Table 1A
Percent Recovery for MS/LCS	Table 1A
Relative Percent Difference of Matrix Duplicate	Table 1A
Other Instrument QC Samples	Table 1A

Laboratories are required to generate laboratory specific performance criteria for LCS element recovery limits, MS/MSD element recovery and relative percent difference ("RPD") limits. These limits must be equal to or fall within the limits specified in Table 1A of this RCP.

~~1.6.2~~ 1.4.3 Specific QA/QC Requirements and Performance Standards for SW-846 Methods 9010/9012/9014

Specific QA/QC requirements and performance standards for SW-846 Methods 9010, 9012, and 9014 are presented in Table 1A. Strict compliance with the QA/QC requirements and performance standards for ~~this method~~these methods, as well as satisfying other analytical and reporting requirements will provide the ~~environmental professional (~~"EP"~~)~~ with "Reasonable Confidence" regarding the usability of analytical data to support ~~DEP~~ environmental decisions. The concept of "Reasonable Confidence" is explained on the CT Department of Energy and Environmental Protection ("DEEP") website.

While optional, parties electing to utilize these protocols will be assured that ~~"~~agency reviewers will, generally accept "Reasonable Confidence~~"~~" data~~, will be generally accepted by agency reviewers. In order to~~. To achieve "Reasonable Confidence" parties must:

1. Comply with the applicable QC analytical requirements prescribed in Table 1A for this test procedure;

2. Evaluate and narrate all protocol non-compliances and implement, as necessary, ~~compliance with~~required corrective actions and analytical response actions for all non-conforming analytical performance standards~~ prescribed in Table 1A for this test method~~; and

3. Retain reported and unreported analytical data and information for a period of 10 years.
~~Adopt the reporting formats and elements specified in Section 1.7 of this method.~~

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Table 1A: Specific QA/QC Requirements and Performance Standards for Methods 9010/9012/9014

Required ~~QA/~~QC Parameter Column 1	Data Quality Objective Column 2	Required Performance Standard Column 3	Required Deliverable Column 4	~~Recommended~~Required Corrective Action Column 5	~~Analytical~~Required Analysis Response ~~Action~~ Column 6	Rationale for Changes
Initial Demonstration of Capability ("IDOC")	Laboratory Analytical Accuracy & Precision	(1) Must be performed prior to using method on samples. (2) Must be performed for each matrix. (3) Must follow procedure in SW-846 9010 and the requirements in Section 1.4.2 of this protocol.	No	Refer to "Initial Demonstration of Capability" Section in the applicable EPA method and Section 1.4.2 of this protocol.	NA	Group accepted MA language without references to specific revision references.
Preparation of Samples	Accuracy and Representativeness	~~All~~(1) For Total CN, all aqueous and solid samples must be distilled/prepared prior to analysis. See ~~Methods~~SW-846 9010, 9013, or Standard Method 4500-CN, for ~~details.~~ appropriate reflux distillation procedures.	No	NA	NA	Group accepted MA language in Column 3 with the exception of the PAC language as CT does not maintain criteria for PAC.
Initial Calibration	Laboratory Analytical Accuracy	(1) ~~For manual colorimetric procedure at least every six months or~~	No	~~Re-optimize~~Perform instrument ~~and~~maintenance as necessary; recalibrate as ~~necessary~~required by	~~Sample analysis cannot proceed without valid~~Suspend all analyses until initial	Group accepted MA language in column 3, item 1 with revision to requiring frequency of

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Required ~~QA/~~QC Parameter Column 1	Data Quality Objective Column 2	Required Performance Standard Column 3	Required Deliverable Column 4	~~Recommended~~Required Corrective Action Column 5	~~Analytical~~Required Analysis Response ~~Action~~ Column 6	Rationale for Changes
		~~whenever ICV fails. For semi-automated procedure, daily~~Frequency: Daily prior to sample analysis. (2) ~~Minimum~~Initial Calibration: minimum of a calibration blank plus five un-distilled KCN calibration standards~~.~~ (3) Low-level standard in calibration must be ~~≤~~at or below the RL~~.~~/LLOQ. High level standard in calibration defines the upper end of the linear calibration range. ~~3~~(4) Linear ~~curve~~regression with ~~"~~correlation coefficient r~~"~~ ≥ 0.995~~.~~ ~~4) Samples and stds matrix matched.~~ (5) If titration procedure is used, the silver nitrate		method.	calibration~~.~~ meets criteria.	calibration to daily rather than based on criteria of QC samples. Maintained the RCP language in Column 3, items 7 & 8

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Required ~~QA/~~QC Parameter Column 1	Data Quality Objective Column 2	Required Performance Standard Column 3	Required Deliverable Column 4	~~Recommended~~Required Corrective Action Column 5	~~Analytical~~Required Analysis Response ~~Action~~ Column 6	Rationale for Changes
		solution must be standardized as ~~in~~ described in "Standard Methods for the Examination of Water and Wastewater," Method ~~SM4500~~4500-CN ~~D (Note 1) every 30 days~~. ~~6~~(7) Samples and standards matrix matched. (8) Stock ~~cyanide~~CN solution must be checked monthly.				
Initial Calibration Verification ("ICV")	Laboratory Analytical Accuracy	(1) Frequency- immediately after each initial calibration. ~~For manual colorimetric and titration procedure, daily and prior to sample analysis. For semi-automated procedure daily immediately after calibration.~~ (2) Prepared using standard source	No	(1) Reanalyze ICV; if acceptable, no further action required. (2) If reanalysis is still outside of criteria, recalibrate and reanalyze ICV. ~~Re-calibrate/Re-analyze ICV as required by method~~	Suspend all analyses until ICV meets criteria.	Group accepted MA language in column 3, items 1, 3, & 4 and Column 5..

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Required ~~QA/~~QC Parameter Column 1	Data Quality Objective Column 2	Required Performance Standard Column 3	Required Deliverable Column 4	~~Recommended~~Required Corrective Action Column 5	~~Analytical~~Required Analysis Response ~~Action~~ Column 6	Rationale for Changes
		different than used for initial calibration (un-distilled). (3) Concentration level near midpoint of curve. (4) Percent recovery must be 85-115%.				
Initial Calibration Blank ("ICB")	Laboratory Analytical Sensitivity (instrument drift & contamination)	(1) Frequency- immediately after ICV (2) Un-distilled. (3) CN must be ≤ ½ RL/LLOQ	No	(1) Reanalyze ICB; if acceptable, no further action required. (2) If reanalysis is still outside of criteria, recalibrate and reanalyze ICV & ICB.	Suspend all analyses until ICB meets criteria.	Group accepted MA language.
Low-Level Calibration Verification ("LLCV")	Laboratory Analytical Sensitivity (verify low-end of calibration range/verify RL/LLOQ)	(1) Frequency- daily prior to sample analysis. If initial calibration. is performed on same day as sample analysis and includes the RL/LLOQ as the low-level standard in the initial calibration curve (as required by calibration), then LLCV is not required. (2) Prepared using same source as initial calibration standards: un-distilled (3) Concentration	No	(1) Reanalyze LLCV; if acceptable no further action required (2) If reanalysis is still outside of criteria and concentrations of CN are ≤10x RL/LLOQ in associated field samples, recalibrate and reanalyze LLCV and associated samples. (3) If concentrations of CN are >10x RL/LLOQ in associated field samples, include explanation in laboratory report narrative no further action required.	Suspend all analyses until LLCV meets criteria. unless the concentrations of CN are >10X RL/LLOQ in the associated field samples.	Group accepted MA language.

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Required ~~QA/~~QC Parameter Column 1	**Data Quality Objective** Column 2	**Required Performance Standard** Column 3	**Required Deliverable** Column 4	**~~Recommended~~Required Corrective Action** Column 5	**~~Analytical~~Required Analysis Response ~~Action~~** Column 6	**Rationale for Changes**
		level must be at the level of the RL/LLOQ for CN. (4) Percent recovery must be 70-130%.				
Continuing Calibration Verification ("CCV")	Laboratory Analytical Accuracy	(1) Every 10 samples and at the end of the analytical ~~sequence.~~run (2) ~~Can be~~ Prepared using same source ~~or second source.~~as initial calibration standards: un-distilled (3) Concentration level near midpoint of curve (4) Percent recovery must be 85-115%	No	~~Recalibrate/Re-analyze~~(1) Reanalyze CCV; if acceptable, no further action required. (2) If reanalysis is still outside of criteria, recalibrate and reanalyze all associated samples since last compliant CCV- unless 3 applies. (3) If recovery is high and all associated sample results are non-detected, no corrective action required.	~~Report non-conformances~~If 3 applies, include explanation in laboratory report narrative. ~~.~~	Group accepted MA language in column 3, items 2-4; Column 5, items 1 & 3; Column 6with the exception of requiring analysis of CCV every 10 samples rather than 20 samples.
Continuing Calibration Blank ("CCB")	Laboratory Analytical Sensitivity (instrument drift & contamination)	(1) Frequency- Every 10 samples following CCV and at the end of the analytical run (2) Un-distilled. (3) CN must be ≤½ RL/LLOQ (4) Matrix matched with standards and samples	No	~~Recalibrate/Re-analyze all samples since last compliant CCB~~ (1) Reanalyze CCB; if acceptable, no further action required. (2) If reanalysis is still outside of criteria, recalibrate and reanalyze all associated samples since last compliant CCB- unless 3 applies.	~~Report non-conformances in narrative.~~ If 3 applies, include explanation in laboratory report narrative.	Group accepted MA language in column 3, item 2; Column 5; and Column 6 with the exception of requiring CCB frequency every 10 samples rather than 20 samples.

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Required ~~QA/~~QC Parameter Column 1	Data Quality Objective Column 2	Required Performance Standard Column 3	Required Deliverable Column 4	~~Recommended~~Required Corrective Action Column 5	~~Analytical~~Required Analysis Response ~~Action~~ Column 6	Rationale for Changes
				(3) If concentration of CN in CCB is > ½ RL/LLOQ but all associated sample results are either non-detected or >10x concentration of CN in CCB, no corrective action required.		
Method Blank	Laboratory Method Sensitivity (contamination evaluation)	(1) Frequency- one per distillation batch of ≤20 field samples (2) Must be distilled with the samples in the batch (3) CN must be ≤½ RL/LLOQ (4) Matrix specific and matrix matched.	Yes	~~Locate source of contamination and correct problem. Reprepare samples unless all detected analyte concentration >10x method blank level~~ (1) Reanalyze MB; if acceptable, no further action required. (2) If reanalysis is still outside of criteria, redistill and reanalyze MB and all associated field samples in batch- unless 3 applies. (3) If concentration of CN in MB is >½ RL/LLOQ but all associated sample results are either non-detected or >10x concentration of CN in MB, no corrective action required.	~~Report non-conformances in case narrative.~~ If 3 applies, include explanation in laboratory report narrative.	Group accepted MA language in Column 3, item 2; Column 5; Column 6.

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Required ~~QA/~~QC Parameter Column 1	Data Quality Objective Column 2	Required Performance Standard Column 3	Required Deliverable Column 4	~~Recommended~~Required Corrective Action Column 5	~~Analytical~~Required Analysis Response ~~Action~~ Column 6	Rationale for Changes
Lab Control Sample ("LCS")	Laboratory Analytical Accuracy	(1) Frequency- one per distillation batch of ≤20 field samples (2) Total CN- LCS must be matrix-matched by distilling with the samples using the same preparation method. It is recommended that a solid SRM be prepared and analyzed with solid field samples as the "solid LCS." An SRM is a soil or sediment matrix that contains CN at a known concentration and with 95% confidence limits. (3) Concentration level for aqueous LCS near midpoint of curve. (4) LCS must be distilled with samples in batch. (5) Percent recovery must be 80-120% for aqueous LCS and within vendor control limits (95%	Yes	~~Redigest and reanalyze all samples.~~ (1) Reanalyze LCS; if acceptable, no further action required. (2) If reanalysis is still outside of criteria and LCSD is in-control for CN, no corrective action required. (3) If LCS and LCSD are both outside of recovery criteria, redistill and reanalyze LCS/LCSD and all associated field samples in batch. (4) Re-digest and reanalyze all samples.	Report non-conformances in laboratory report narrative.	Group accepted MA language in Column 3, items 2-5; Columns 5 & 6.

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Required ~~QA/~~QC Parameter Column 1	Data Quality Objective Column 2	Required Performance Standard Column 3	Required Deliverable Column 4	~~Recommended~~Required Corrective Action Column 5	~~Analytical~~Required Analysis Response ~~Action~~ Column 6	Rationale for Changes
		confidence limits) for solid LCS. (6) Standard source different from initial calibration source. (7) Matrix specific (solid, aqueous, etc.).				
LCS Duplicate ("LCSD")	Laboratory Analytical Accuracy & Precision	(1) Frequency – One per distillation batch of <20 field samples ONLY if not performing project-specific MD. (2) LCS Duplicate must be matrix-matched by distilling with the samples using the same preparation method. It is recommended that a solid SRM be prepared and analyzed with solid field samples as the "solid LCS." An SRM is a soil or sediment matrix that contains CN at a known concentration and with 95% confidence limits. (3) Concentration levels must be same	Yes	(1) Reanalyze LCSD; if acceptable, no further action required. (2) If reanalysis is still outside of recovery criteria for CN, and LCS is incontrol for CN recovery, no corrective action required. (3) If LCSD and LCS are both outside of recovery criteria, redistill and reanalyze LCS/LCSD and all associated field samples in batch.	Report recovery and RPD non-conformances in laboratory report narrative.	Group accepted MA language

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Required ~~QA/~~QC Parameter Column 1	Data Quality Objective Column 2	Required Performance Standard Column 3	Required Deliverable Column 4	~~Recommended~~Required Corrective Action Column 5	~~Analytical~~Required Analysis Response ~~Action~~ Column 6	Rationale for Changes
		as LCS. (4) LCS Duplicate must be distilled with samples in batch. (5) Percent recovery must be 80-120% for aqueous LCS and within vendor control limits (95% confidence limits) for solid LCS. (7) RPDs must be <20% for aqueous LCS/LCSD and <30% for solid LCS/LCSD.				
Matrix Spike ("MS") Site-Specific	Method Accuracy in Sample Matrix	(1) Frequency- One per distillation batch of ≤20 field samples per matrix strongly recommended (designated by data user on COC or at project set-up). (2) Percent recovery must be 75-125%	Yes (if requested by the data user) ~~If analyzed)~~	~~None~~ (1) Reanalyze MS; if acceptable, no further action required. (2) After reanalysis, if MS recovery is 30-74% or >125% and LCS was in control, no corrective action required. (3) If recovery is 30% and associated with non-detected results, redistill (homogenize sample well) and reanalyze sample/MS pair. Report results and narrate.	~~Note outliers in narrative~~ Report non-conformances laboratory report narrative. If re-digested due to recoveries <30%, report both sets of sample/MS data.	Group accepted MA language in Columns 3, item 1; Columns 5 & 6.
Matrix Duplicate ("MD")	Method Precision in Sample Matrix	(1) Frequency- one per distillation batch	Yes (if requested	~~If LCS meets criteria, narrate outliers.~~	~~Note outliers in narrative~~	Group accepted MA in Column 3, item 2;

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Required ~~QA/~~QC Parameter Column 1	Data Quality Objective Column 2	Required Performance Standard Column 3	Required Deliverable Column 4	~~Recommended~~Required Corrective Action Column 5	~~Analytical~~Required Analysis Response ~~Action~~ Column 6	Rationale for Changes
Site-Specific		of ≤20 field samples per matrix is strongly recommended (designated by data user on COC or at project set-up). (2) Prepare by distilling and analyzing an additional aliquot of the same field sample used for MS. (3) RPD for CN must be ≤20% for aqueous and ≤30% for solids.	by data user). ~~(If analyzed)~~	Narrate	Report non-conformances in laboratory report narrative.	Column 5 & 6.
General Reporting Issues	NA	(1) Non-detected values must be reported with the sample-specific RL/LLOQ for Total CN and using all appropriate preparation/dilution factors. (2) The lab must only report values ≥ the sample-specific RL/LLOQ. Concentrations below the RL/LLOQ should be reported as "ND" with the sample-specific RL/LLOQ	~~Yes~~ NA	NA	(1) The performance of dilutions must be documented in the laboratory report narrative or on the report form. Unless due to elevated concentrations of CN, reasons for dilutions must be explained in the laboratory report narrative. (2) If samples are not preserved properly or are not received with an acceptable cooler	Group accepted MA language in Column 3, items 1 & 3; Column 6.

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Required ~~QA/~~QC Parameter Column 1	Data Quality Objective Column 2	Required Performance Standard Column 3	Required Deliverable Column 4	~~Recommended~~Required Corrective Action Column 5	~~Analytical~~Required Analysis Response ~~Action~~ Column 6	Rationale for Changes
		also reported. (3) Sample concentrations that exceed the highest calibration standard must be diluted and reanalyzed to fall within the linear calibration range. (4) Results for soils/sediments must be reported on a dry-weight basis for comparison to RSR regulatory standards.			temperature, not the non-conformances in the laboratory report narrative. (3) If samples are distilled or analyzed outside of the holding time, not the non-conformances in the laboratory report narrative. (4) Narrate any additional method non-compliance or sample-specific anomaly.	
						If the RL/LLOQ is estimated due to unacceptable recovery of the lowest standard, the RL/LLOQ has not been achieved; Question 5b of the "Reasonable Confidence Protocol Laboratory Analysis QA/QC Certification Form" must be answered "NO" and this must be addressed in the laboratory report

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Required ~~QA/~~QC Parameter Column 1	Data Quality Objective Column 2	Required Performance Standard Column 3	Required Deliverable Column 4	~~Recommended~~Required Corrective Action Column 5	~~Analytical~~Required Analysis Response ~~Action~~ Column 6	Rationale for Changes
						narrative. Standard Methods for the Examination of Water and Wastewater, 20th ed, APHA-AWWA-WEF. Footnotes for Table 1A * Refers to latest promulgated version of SW-846 Method 9010/9012/9014. r = Correlation Coefficient RPD = Relative Percent Difference %RSD = Relative Percent Standard Deviation N/A = Not Applicable 1. Standard Methods for the Examination of

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Required ~~QA/~~QC Parameter Column 1	Data Quality Objective Column 2	Required Performance Standard Column 3	Required Deliverable Column 4	~~Recommended~~Required Corrective Action Column 5	~~Analytical~~Required Analysis Response ~~Action~~ Column 6	Rationale for Changes
						Water and Wastewater, 20th ed, APHA-AWWA-WEF.

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~~1.8~~1.5 Routine Reporting Deliverables for Method 9010/9012/9014

The following table (Table ~~1.2~~4.0) lists the routine report deliverables. Note that while laboratories are not required to report certain items, they must keep the data on file and may be required to report all items in special circumstances.

Table 4.0: Report Deliverables

Parameter	Deliverable	Comments
Sample Preparation Data	NO	Data on file at laboratory
Initial Calibration	NO	Correlation coefficient must meet QA/QC requirements
Initial Calibration Verification Standard	NO	ICV must pass
Initial Calibration Blank	NO	Note non-conformances in laboratory report narrative
Continuing Calibration Verification	NO	CCV must pass
Continuing Calibration Blank	NO	Note non-conformances in laboratory report narrative
Method Blanks	YES	Note non-conformances in laboratory report narrative. Flag all positive sample results above RL/LLOQ with “B” flag.
Lab Control Sample / Lab Control Sample Duplicate	YES	Note non-conformances in laboratory report narrative
Site Specific Matrix Spike/ Matrix Duplicate	YES (If requested)	Note non-conformances in laboratory report narrative
General Reporting Issues	YES	Note non-conformances in laboratory report narrative
QA/QC Certification Form	YES	Signed by laboratory director or their designee.
Chain-of-Custody Form	YES	Signed by sample collector, courier, and laboratory.

~~1.8~~1.5.1 Reporting and Flagging of Results

The following rules apply to reporting results:

- Non-Detects: Report all non-detects and results below the reporting limit as “ND” (Not Detected at the specified ~~Reporting Limit~~RL/LLOQ). The ~~reporting limit for each compound~~RL/LLOQ in each sample must be listed on the report and ~~take into account~~based upon the lowest calibration standard, the exact sample mass, any dilution factors, percent moisture, etc.
- ~~Compounds detected~~Detections above the ~~reporting limit~~RL/LLOQ in blanks and found in samples, also above the ~~reporting limit~~RL/LLOQ, shall be flagged with a “B” suffix (e.g~~.~~., 25B~~).~~)
- All soil/sediment results shall be reported on a dry weight basis.

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1.6 Sample Containers, Preservations, and Holding Times

Table 5.0 identifies the type of containers, preservation requirements, and holding times dependent upon analyte and matrix.

Table ~~2A~~5.0: Sample Containers, Preservations, and Holding Times

Matrix	Container[1,2]	Preservative[3]	Holding Time
Aqueous (No chlorine present)	500 mL plastic or glass	Sodium or potassium hydroxide to pH >12	14 days to distillation; analyze distillates within 24 hours of distillation
Aqueous (Chlorine present)	500 mL plastic or glass	(1) Neutralize chlorine with either sodium arsenite, sodium thiosulfate, or ascorbic acid. (2) Add sodium or potassium hydroxide to pH >12	14 days to distillation; analyze distillates within 24 hours of distillation
Soil/Sediment samples.	250 mL plastic or glass jar with Teflon or plastic lined cap.	Cool to 4 ± 2º C	14 days to distillation; analyze distillates within 24 hours of distillation
High Concentration Waste Samples	Collect in amber glass jar with Teflon or plastic lined cap.	Cool 4 ± 2º C. Protect from light	14 days to distillation; analyze distillates within 24 hours of distillation

[1]The number of sampling containers specified is not a requirement. For specific analyses, the collection of multiple sample containers is encouraged to avoid resampling if sample is consumed or compromised during shipping and/or analysis.

[2]Plastic bottles must be either high density polyethylene or Teflon

[3]If samples were received by the laboratory on the same day of collection and were stored and transported to the laboratory on ice, cooler temperatures above 6ºC are acceptable.