

State Of Connecticut
Department of Environmental Protection

Recommended Reasonable Confidence Protocols

Quality Assurance and Quality Control Requirements

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

Version 2.0
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Written by the Connecticut DEP QA/QC Workgroup

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1.0 QA/QC Requirements for Methods 9010/9012/9014

1.1 Method Overview

Method 9010 is a distillation procedure for cyanide. The distillation procedure breaks down most metallo-cyanide complexes and removes the cyanide from most potential interferences. After distillation the cyanide may be determined using the colorimetric or titration procedure found in Method 9014. Method 9012 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 Method

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.

1.2.2 In the colorimetric measurement, the cyanide is converted to cyanogen chloride (CNCl) by reaction of cyanide with chloramine-T at a pH less than 8. After the reaction is complete, color is formed on 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. 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 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 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 limit.

1.3 Reporting Limits for Methods 9010/9012/9014

The reporting limit (RL) for the colorimetric method is based upon the lowest standard in the calibration curve corrected for specific sample weight or volume, moisture content (for soils/sediments), and any dilutions. The RL 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. In order to use the titrametric procedure for aqueous samples, the cyanide concentration must be high enough to require 0.20 mLs silver nitrate (after blank subtraction). For soil samples the titrametric procedure may be used as long as the RL for a 0.20 mL net titration is below the detection limit required.

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.

1.4 Interferences

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

1.4.2 Oxidizing agents such as chlorine decompose most cyanides. Chlorine interferences can be removed by adding an excess of sodium arsenite or other agent (see Table 2A) to the sample prior to preservation with base to reduce the chlorine to chloride which does not interfere.

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 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.

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 for an extraction procedure to eliminate this interference.

1.5 General Quality Control Requirements

Each laboratory is required to operate a formal quality assurance program and be certified by the Connecticut Department of Public Health for the analysis performed. The minimum requirements include initial demonstration of laboratory proficiency, ongoing analysis of standards and blanks to confirm acceptable continuing performance, and analysis of laboratory control samples (LCS) to assess precision and accuracy. The use of site specific matrix spikes and matrix duplicates is highly recommended. Evaluation of sample matrix effects on mercury recovery is key to making good decisions.

Laboratories must document and have on file an Initial Demonstration of Proficiency for each combination of sample preparation and determinative method being used. These data must meet or exceed the performance standards as presented in Section 1.5 and Table 1A. See Section 4.4.1 of SW-846 Chapter One for the procedure. The Initial Demonstration of Proficiency must include the following elements:

Table 1.1 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

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

1.6.1 General Quality Control Requirements for Determinative Inorganic Methods

Refer to SW-846 Chapter One for general quality control procedures for all inorganic methods, including SW-846 Methods 9010/9012/9014. These requirements ensure that each laboratory maintain a formal quality assurance program and records to document the quality of all inorganic data.

Quality Control procedures necessary to evaluate the instrument's operation may be found in Chapter One, Section 2.0, and include evaluation of calibrations and performance of sample analyses.

1.6.2 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 9010/9012/9014 are presented in Table 1A. Strict compliance with the QA/QC requirements and performance standards for this method, 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 decisions.

While optional, parties electing to utilize these protocols will be assured that "Reasonable Confidence" data, will be generally accepted by agency reviewers. In order 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, as necessary, compliance with performance standards prescribed in Table 1A for this test method; and
3. Adopt the reporting formats and elements specified in Section 1.7 of this method.

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

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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.

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

Required QA/QC Parameter	Data Quality Objective	Required Performance Standard	Required Deliverable	Recommended Corrective Action	Analytical Response Action
Preparation of Samples	Accuracy and Representativeness	All samples must be distilled prior to analysis. See Methods 9010 for details.	NO		
Initial Calibration	Laboratory Analytical Accuracy	1) For manual colorimetric procedure at least every six months or whenever ICV fails. For semi-automated procedure, daily prior to sample analysis. 2) Minimum of calibration blank plus five calibration standards. Low standard must be \leq RL. 3) Linear curve with "r" \geq 0.995. 4) Samples and stds matrix matched. 5) If titration used, silver nitrate must be standardized as in Method SM4500-CN D (Note 1) every 30 days. 6) Stock cyanide solution must be checked monthly.	NO	Re-optimize instrument and recalibrate as necessary.	Sample analysis cannot proceed without valid initial calibration.
Initial Calibration Verification (ICV)	Laboratory Analytical Accuracy	1) For manual colorimetric and titration procedure, daily and prior to sample analysis. For semi-automated procedure daily immediately after calibration. 2) 2 nd source std distilled with batch mid-range or vendor supplied value. 3) ICV \pm 15% of true value.	NO	Re-calibrate/Re-analyze ICV as required by method.	Suspend all analyses until problem corrected and ICV meets criteria.
Continuing Calibration Verification (CCV)	Laboratory Analytical Accuracy	1) Every 10 samples and at end of analytical sequence. 2) Can be same source or second source. 3) Recovery \pm 15% of true value	NO	Recalibrate/Re-analyze all samples since last compliant CCV	Report non-conformances in narrative.

Table 1A Specific QA/QC Requirements and Performance Standards for Methods 9010/9012/9014* (continued)

Required QA/QC Parameter	Data Quality Objective	Required Performance Standard	Required Deliverable	Recommended Corrective Action	Analytical Response Action
Continuing Calibration Blank (CCB)	Evaluation of instrument drift, sensitivity, and contamination.	1) Every 10 samples immediately after CCV. 2)) Matrix matched with standards and samples. 3) CCB must be < RL	NO	Recalibrate/Re-analyze all samples since last compliant CCB	Report non-conformances in narrative.
Method Blanks	Laboratory Contamination Evaluation	1) Digested every 20 or every batch, whichever is greater. 2) Matrix specific and matrix matched 3) Cyanide must be <RL	YES	Locate source of contamination and correct problem. Reprepare samples unless all detected analyte concentration >10x method blank level	Report non-conformances in case narrative.
Laboratory Control Sample (LCS)	Laboratory Method Accuracy	1) Every 20 samples or each batch, whichever is more frequent 2) Standard source different from initial calibration source. 3) Matrix specific (solid, aqueous, etc). 4) LCS recoveries $\pm 20\%$ for aqueous media and within vendor control (95% confidence limits) for solids.	YES	Redigest and reanalyze all samples.	Report non-conformances in narrative.
Site Specific Matrix Spike	Accuracy in Sample Matrix	1) Every 20 samples or batch per matrix** 2) Percent recovery limits must be between 75-125%.	Yes**(If analyzed)	None	Note outliers in narrative

Table 1A Specific QA/QC Requirements and Performance Standards for Methods 9010/9012/9014* (continued)

Required QA/QC Parameter	Data Quality Objective	Required Performance Standard	Required Deliverable	Recommended Corrective Action	Analytical Response Action
Site Specific Matrix Duplicate	Precision in Sample Matrix	1) Every 20 samples or batch per matrix** 2) For aqueous samples RPD ≤ 20% 3) For solids RPD ≤ 35%	Yes** (If analyzed)	If LCS in criteria, narrate outliers.	Note outliers in narrative
General Reporting Issues	N/A	1) The laboratory should report only concentrations detected above the sample specific RL. 2) Concentrations below the reporting limit (RL) should be reported as “ND” with the sample specific RL also reported 3) Dilutions: If analyte above linear range, dilute and reanalyze for those analytes. 4) Soils/sediments reported on a dry weight basis. 5) RL must be verified daily with a low level calibration standard the RL. Must be part of initial calibration.	YES	N/A	

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 Water and Wastewater, 20th ed, APHA-AWWA-WEF.

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. 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.

1.8 Routine Reporting Deliverables for Method 9010/9012/9014

The following table (Table 1.2) 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.

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). The reporting limit for each compound in each sample must be listed on the report and take into account the exact sample mass, any dilution factors, percent moisture, etc.

Compounds detected above the reporting limit in blanks and found in samples, also above the reporting limit, shall be flagged with a “B” suffix (e.g. 25B).

All soil/sediment results shall be reported on a dry weight basis.

Table 1.2 Report Deliverables

PARAMETER	DELIVERABLE	COMMENTS
Sample Preparation Data	NO	
Initial Calibration	NO	
Initial Calibration Verification Standard (ICV)	NO	ICV must pass
Initial Calibration Blank (ICB)	NO	Note non-conformances in narrative
Continuing Calibration Verification (CCV)	NO	CCV must pass
Method Blanks	YES	Note non-conformances in narrative. Flag all positive sample results above RL with "B" flag.
Lab Control Sample (LCS)	YES	Note non-conformances in narrative
Site Specific Matrix Spike/ Matrix Duplicate	YES (If requested)	Note non-conformances in narrative
General Reporting Issues	YES	Note non-conformances in narrative
QA/QC Certification Form	YES	Signed by laboratory director or his/her designee.

Table 2A Sample Containers, Preservation, and Holding Times

MATRIX	CONTAINER	PRESERVATIVE	HOLDING TIME
Aqueous (No chlorine present)	500 mL plastic† or glass	Sodium or potassium hydroxide to pH >12	14 days
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
Soil/Sediment samples.	250 mL plastic or glass jar with Teflon or plastic lined cap.	Cool to 4 ± 2° C	14 days
High Concentration Waste Samples	Collect in amber glass jar with Teflon or plastic lined cap.	Cool 4 ± 2° C. Protect from light	14 days

Notes:

† Plastic bottles must be either high density polyethylene or Teflon