WSC – CAM – VI A

Quality Control Requirements and Performance Standards for the **Analysis of Total Cyanide and Physiologically Available Cyanide (PAC)** in Support of Response Actions under the Massachusetts Contingency Plan (MCP)

VI. Miscellaneous Wet Chemical Methods

A. Quality Control Requirements and Performance Standards for WSC-CAM-VI A (Total Cyanide and Physiologically Available Cyanide)

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ACRONYM LIST

CAM	Compendium of Analytical Methods
CASN	Chemical Abstracts Service Number
CCB	Continuing calibration blank
CCV	Continuing calibration verification
CN	Cyanide
CN^-	Cyanide ion (Free Cyanide)
CNCl	Cyanogen chloride
HCl	Hydrochloric acid
HCN	Hydrocyanic acid
HNO_3	Nitric acid
LLCV	Low-level calibration verification
ICB	Initial calibration blank
ICV	Initial calibration verification
IDP	Initial demonstration of proficiency
IRAs	Immediate Response Actions
LCS/LCSD	Laboratory control sample / Laboratory control sample duplicate
LR	Linear range
MassDEP	Massachusetts Department of Environmental Protection
MB	Method blank
MCP	Massachusetts Contingency Plan
MD	Matrix duplicate
MDL	Method detection limit
MS	Matrix spike
MOHML	Massachusetts Oil and Hazardous Materials List
NaOH	Sodium hydroxide
PAC	Physiologically Available Cyanide
%D	Percent difference
%R	Percent recovery
r	Correlation coefficient
RAO	Response Action Outcome
RCs	Reportable Concentrations
RL	Reporting limit
RPD	Relative percent difference
RQs	Reportable Quantities
QA	Quality assurance
QC	Quality control

UNITS:

g	Gram
mg	Milligram
mg/L	Milligram per liter
mg/Kg	Milligram per kilogram
mL	Milliliter
nm	nanometer
µg/L	Microgram per liter
µm	Micrometer

1.0 Quality Control Requirements and Performance Standards for WSC-CAM-VI A

1.1 Overview of WSC-CAM-VI A

WSC-CAM-VI A, *Quality Control Requirements and Performance Standards for the Analysis of Total Cyanide and Physiologically Available Cyanide (PAC) in Support of Response Actions under the Massachusetts Contingency Plan (MCP)*, is a component of MassDEP's Compendium of Analytical Methods (CAM). Effective July 1, 2010, this revised CAM protocol, WSC-CAM-VI A, replaces the original Cyanide CAM document, WSC-CAM-VI A (effective date, August 13, 2004). Refer to WSC-CAM-I A for an overview of the CAM process. Please note that while this protocol must be followed on and after the effective date of July 1, 2010 for the purpose of "Presumptive Certainty," the revised protocol may be used optionally prior to its effective date upon its publication on April 15, 2010.

This document provides Quality Control (QC) requirements and performance standards to be used in conjunction with the required analytical methods SW-846 9014 (manual colorimetric using UV spectrometry), SW-846 9012B (automated colorimetric using UV spectrometry), or Standard Method 4500-CN^- (manual colorimetric using UV spectrometry; *Standard Methods for the Examination of Water and Wastewater*, Part 4000, 20th Edition), for the analysis of aqueous and solid samples for Total Cyanide and Physiologically Available Cyanide (PAC). The QC requirements and performance standards specified in this document in Table VI A-1 together with the analytical procedures described in the referenced methods constitute the WSC-CAM-VI A protocol. All protocols included in the CAM are considered "methods" published by the MassDEP pursuant to the provisions of 310 CMR 40.0017(2). Use of EPA SW-846 9014, 9012B, or Standard Method 4500-CN^- is a "Presumptive Certainty" requirement of WSC-CAM-VI A. Sample preservation, container and analytical holding time specifications for aqueous, soil, and sediment matrices for Cyanide analyzed in support of MCP decision-making are presented in Appendix VI A-1 of this document and Appendix VII-A of WSC-CAM-VII A *Quality Assurance and Quality Control Guidelines for the Acquisition and Reporting of Analytical Data in Support of Response Actions Conducted Under the Massachusetts Contingency Plan (MCP)*. Data reporting requirements are also provided in WSC-CAM-VII A.

Overall usability of data produced using this CAM protocol should be evaluated for compliance with project-specific data quality objectives, regardless of "Presumptive Certainty" status. For more guidance on data usability, refer to MassDEP Policy #WSC-07-350, *MCP Representativeness Evaluations and Data Usability Assessments*.

1.1.1 Reporting Limits for Cyanide by WSC-CAM-VI A

The reporting limit (RL) for Cyanide using WSC-CAM-VI A 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, etc., as required. The CAM RLs for Cyanide using the WSC-CAM-VI A protocol are:

- 0.005-0.010 mg/L for aqueous samples (surface water, groundwater, and drinking water); and
- 1.0 mg/Kg for soil/sediment samples (assuming 100% solids).

For "Presumptive Certainty" purposes, if the typical CAM RLs are not achieved, respond "NO" to Question G of the "MassDEP MCP Analytical Protocol Certification Form" and address the CAM RL exceedance in the laboratory narrative.

Reporting limits lower than the above-referenced CAM RLs for Cyanide may be required to satisfy project requirements. The RL (based on the concentration of the lowest calibration standard or the LLCV) for Cyanide must be less than or equal to the MCP standards or criteria that the contaminant concentrations are being compared to (e.g., Method 1 Standards, benchmark values, background, etc.). Meeting MCP standards or criteria may require analytical modifications to improve sensitivity. All such modifications must be described in the laboratory narrative.

1.1.2 Initial Demonstration of Proficiency for WSC-CAM-VI A

Each laboratory that uses the WSC-CAM-VI A protocol is required to operate a formal quality assurance program. The minimum requirements of this program consist of an initial demonstration of laboratory proficiency, ongoing analysis of standards and blanks to confirm acceptable continuing performance, the preparation/analysis of laboratory control samples (LCS) and/or matrix spikes (MS) to assess accuracy and LCS duplicates or matrix duplicates (MD) to assess precision.

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 Table VI A-1 of this protocol. General requirements for performing the Initial Demonstration of Proficiency can be found in SW-846 Chapter One and Section 8 of SW-846 Methods 9010C, 9012B, and 9014. The procedure in Section 8.6 of SW-846 Method 9010C must be followed. The data associated with the Initial Demonstration of Proficiency must be kept on file at the laboratory and made available to potential data users on request. The data associated with the Initial Demonstration of Proficiency for WSC-CAM-VI A must include the following:

QC Element	Performance Criteria
Initial Calibration	See WSC-CAM-VI A, Table VI A-1, for Performance Criteria
Continuing Calibration	
Method Blanks	
Percent Recovery for Total CN: LCS & MS PAC: LCS-P, LCS-N, & MS	
Relative Percent Difference (RPD) for Total CN: LCS Duplicate (LCSD) or MD PAC: LCSD-P, LCSD-N or MD	
High Concentration Distilled Standard	±10% of true value
Low Concentration Distilled Standard	

Laboratories are encouraged to actively monitor pertinent QC performance standards described in Table VI A-1 to assess analytical trends (i.e., systematic bias, etc) and improve overall method performance by preempting potential non-conformances.

For the WSC-CAM-VI A protocol, laboratory-specific control limits must meet or exceed (demonstrate less variability than) the performance standards for each QC element listed in Table VI A-1. It should be noted that the performance standards listed in Table VI A-1 are based on multiple-laboratory data, which are in most cases expected to demonstrate more variability than performance standards developed by a single laboratory.

This protocol is restricted to use by, or under the supervision of, analysts who are experienced in using colorimetric UV spectrometry as a quantitative tool for environmental analyses and knowledgeable in the minimization of interferences described in this method.

1.2 Summary of Cyanide Methods

The following determinative methods may be used for analysis of Total Cyanide or PAC in solution/distillates with WSC-CAM-VI A:

- SW-846 Method 9014 – manual colorimetric UV spectrometry for the determination of free (non-complexed) Cyanide (CN^-) and hydrocyanic acid (HCN) in solution/distillates.
    - This method also includes titrimetric determination; however, the sensitivity of the titrimetric method may not meet data quality objectives (see Section 1.6 of this WSC-CAM-VI A protocol for further information)
- SW-846 Method 9012B – 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

The definitions of different Cyanide species are defined as follows.

- Total Cyanide includes Free Cyanide 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 9010C.

- Free Cyanide (non-complexed) is defined as the sum of cyanide, as hydrocyanic acid (HCN), and cyanide ion (CN^-). Free Cyanide may be determined directly using SW-846 Method 9213 without reflux distillation. Alternatively, SW-846 Method 9213 can be used to measure free cyanide in distillates, with higher RLs than SW-846 Method 9014 (see Section 1.6 of this WSC-CAM-VI A protocol for further details).

- Physiologically Available Cyanide (PAC) as determined by the MassDEP PAC protocol, includes biologically available cyanides that are released during this modified distillation including free cyanide, simple cyanide salts, and some metal-cyanide complexes that are easily dissociated. This protocol will **not** release iron-cyanide complexes from samples.

Cyanides are released from samples using reflux-distillation (see Section 1.3 below), which results in HCN in the distillate. The distillate is treated with chloramine-T at pH <8 to convert the HCN into cyanogen chloride (CNCl) and color is formed by adding pyridine-barbituric acid. Quantitation of Cyanide in the treated distillates is based on the color absorption at 578-nm wavelength using a UV spectrometer.

Absorbance (peak height) is measured as a function of Cyanide concentration, based on a multi-level calibration curve.

Prior to analysis, the aqueous and solid (soil/sediment) samples must be prepared and distilled according to the procedures described in Section 1.3 below.

1.3 Sample Distillation/Preparation Methods for WSC-CAM-VI A

The aggressiveness of the sample digestion associated with the preparation method selected determines the range of cyanide salts and insoluble cyanide complexes that will ultimately be decomposed and captured in the absorber solution and detected by the selected determinative method. Total Cyanide prepared using SW-846 Method 9010C is the most aggressive preparation procedure (measuring almost all cyanide forms), while the MassDEP PAC Protocol, simulating the human digestive system, is the least aggressive preparation procedure (measuring only simple cyanides and excluding iron-cyanide complexes).

Samples for analysis by WSC-CAM-VI A must be prepared/distilled using one of the following methods.

Preparation / Distillation Method	Matrix	Description
SW-846 9010C	Aqueous/Leachate/Waste	*Total and Amenable Cyanide: Distillation* Reflux-distillation for acidic extraction of all forms of Cyanide for Total Cyanide in distillate (as HCN). Macro and Micro-distillation procedures are allowed by modifying reagent volumes.
MassDEP PAC Protocol	Aqueous/Soil/Sediment/Waste	*MassDEP Physiologically Available Cyanide (PAC) Protocol* Reflux-distillation for mildly-acidic extraction of free CN, simple CN salts and other biologically available cyanides for PAC in distillate (as HCN). The PAC protocol does not extract iron-cyanide complexes ("Prussian Blue"). Macro and Micro-distillation procedures are allowed by modifying reagent volumes.
Standard Method 4500-CN^- C	Aqueous/Soil/Sediment/Waste	*Total Cyanide After Distillation* Reflux-distillation for acidic extraction of all forms of CN for Total CN in distillate (as HCN). This method is equivalent to SW-846 Method 9010C.
SW-846 9013	Solids and Oily Waste	*Cyanide Extraction Procedure for Solids and Oils* Sample is first extracted with water at pH ≥10 and then distilled using SW-846 Method 9010C.

1.4 Method Interferences

Refer to Section 3.0 of SW-846 Method 9010C 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 Cyanide (SW-846 Method 9010C and Standard Method 4500-CN^- C). Several common interferences and corrective measures are summarized as follows.

- Oxidizing agents such as chlorine decompose most cyanide compounds and complexes. Chlorine interferences can be removed by adding an excess of ascorbic acid or sodium arsenite to aqueous samples prior to preservation and storage to reduce the chlorine (Cl_2) to non-interfering chloride (Cl^-).
- Sulfide interference can be removed by adding an excess of bismuth nitrate to the samples (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.
- Positive interferences for cyanide (high bias results) may be obtained for samples that contain nitrate and/or nitrite at concentrations exceeding 10 mg/L. During the distillation, nitrate and nitrite will form nitrous acid, which will react with some organic compounds to form oximes. These compounds will decompose under test conditions to generate hydrocyanic acid (HCN). The possibility of interference by nitrate and nitrite is eliminated by pretreatment with sulfamic acid just before distillation.
- Fatty acids, detergents, surfactants, and other compounds may cause foaming during the distillation when they are present in high concentrations. Refer to Section 6.7 of Method SW-846 9010C for an extraction procedure to eliminate this interference.
- 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 greater to minimize this potential interference as described in SW-846 Method 9013, *Cyanide Extraction Procedure for Solids and Oils**.***

1.5 Quality Control Requirements for WSC-CAM-VI A

1.5.1 General QC Requirements

For general quality control procedures for all inorganic methods, including SW-846 Methods 9012B and 9014, refer to SW-846 Chapter One. General QC procedures to evaluate the instrument's operation can also be found in SW-846 Chapter One, Section 2.0, and include evaluation of calibrations and performance of sample analyses.

1.5.2 Specific QC Requirements and Performance Standards for WSC-CAM-VI A.

Specific QC requirements and performance standards for Cyanide using the WSC-CAM-VI A protocol are presented in Table VI A-1. Refer to WSC-CAM-VII A for field QC requirements. ***Note that a project-specific matrix spike (MS) must be performed for total Cyanide and PAC to evaluate accuracy in a solid matrix (soil/sediment) at a frequency of one per 20 samples per matrix***. Strict compliance with the QC requirements and performance standards, as well as satisfying the CAM's other analytical and reporting requirements will provide a data user with "Presumptive Certainty" in support of Response Actions under the MCP. The concept of "Presumptive Certainty" is explained in detail in Section 2.0 of WSC-CAM-VII A.

While optional, parties electing to utilize these protocols will be assured of "Presumptive Certainty" of data acceptance by agency reviewers. In order to achieve "Presumptive Certainty" for analytical data, parties must:

(a) Use the analytical method specified for the selected CAM protocol;

(b) Incorporate **all** required analytical QC elements specified for the selected CAM protocol;
(c) Implement, as necessary, required corrective actions and analytical response actions for **all** non-conforming analytical performance standards;
(d) Evaluate and narrate, as necessary, **all** identified CAM protocol non-compliances; and
(e) Comply with **all** the reporting requirements specified in WSC-CAM-VII A, including retention of reported and unreported analytical data and information for a period of ten (10) years.

In achieving "Presumptive Certainty" status, parties will be assured that analytical data sets:

- ✓ Satisfy the broad QA/QC requirements of 310 CMR 40.0017 and 40.0191 regarding the scientific defensibility, precision and accuracy, and reporting of analytical data; and

- ✓ May be used in a data usability and representativeness assessment, as required in 310 CMR 40.1056(2)(k) for Response Action Outcome (RAO) submittals, consistent with the guidance described in MassDEP Policy #WSC-07-350, *MCP Representativeness Evaluations and Data Usability Assessments*.

1.6 Special Analytical Considerations for WSC-CAM-VI A

- Matrix Spike (MS) Recovery – ***A MS is required for WSC-CAM-VI A for Total Cyanide and PAC in solid matrices (soil/sediment) at a frequency of one per 20 samples per matrix***. Consistent with USEPA Region I data validation guidance, MassDEP requires rejection of non-detected metals results with <30% recovery in the MS. If the MS recovery is <30% and non-detected results were found, the laboratory must follow the required corrective actions listed on Table VI A-1.
    - Laboratories are not required to monitor whether or not matrix spikes are performed on soil/sediment samples at a frequency of one per 20 samples per matrix. This is the responsibility of the data user.
    - For "Presumptive Certainty" purposes, if the data user does not submit a soil/sediment sample for MS analysis, Question H of the "MassDEP MCP Analytical Protocol Certification Form" must be answered NO and this must be noted in the laboratory narrative.
- RLs, sensitivity, and/or the optimum linear concentration range can vary with the cyanide compound or complex, sample matrix and laboratory operating conditions.
- Ion-selective electrode analysis by SW-846 Method 9213 or the titrimetric analysis by SW-846 Method 9014 may be used in place of the colorimetric spectrometry method for samples with high levels of Cyanide (>0.01 mg/L for SW-846 Method 9213 and >0.1 mg/L for SW-846 Method 9014). Data users should note that these analytical methods are not sensitive enough to meet the lowest MCP Method 1 Cleanup Standards for Cyanide.
- The RCRA-defined "reactive" cyanide content of a waste (the cyanide content that could generate toxic fumes when exposed to mild acidic conditions) is not determined by this WSC-CAM-VI A protocol. Refer to Chapter Seven of SW-846 for additional information on reactive cyanide.
- 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 and the standards to obtain colors of comparable intensity.
- Some cyanide complexes, such as Potassium Ferricyanide, K_3 [Fe-$(CN)_6$], may be susceptible to photodegradation when exposed to fluorescent lighting or sunlight during sample handling

and/or analysis. This photodegradation can change the type of the cyanide compounds in the sample, which is critical for the PAC method (such a change will not affect Total CN measurements). Therefore, if PAC is being measured, due caution must be exercised to limit the exposure of the sample to light to maintain the integrity of sample from collection through analysis.

1.7 Analyte List for WSC-CAM-VI A

The MCP analyte list for WSC-CAM-VI A consists of Cyanide, CASN 57-12-5, as measured in distillates for either Total Cyanide or PAC.

It is the responsibility of the data user, in concert with the laboratory, to establish the range and required RL for the target analytes. Sources of various MassDEP standards and criteria are as follows:

- Reportable Quantities (RQs) and Concentrations (RCs) as described in 310 CMR 40.1600, The Massachusetts Oil and Hazardous Materials List (MOHML), in Subpart P of the MCP may be found at the following URL: https://www.mass.gov/site-cleanup-regulations-policies-forms-more.
- An online searchable Oil & Hazardous Materials List of RQs and RCs values may be found at the following URL: https://www.mass.gov/service-details/oil-hazardous-material-list.
- An updated list of MCP Method 1 Standards may be found at the following URL: https://www.mass.gov/site-cleanup-regulations-policies-forms-more.

Cyanide, expressed as Physiologically Available Cyanide (PAC), has promulgated MCP Method 1 groundwater/soil standards. In the absence of PAC data, the MCP standards are applicable to Total Cyanide.

Table VI A-1: Specific QC Requirements and Performance Standards for Total Cyanide and PAC using WSC-CAM-VI A

Required QC Parameter	Data Quality Objective	Required Performance Standard	Required Deliverable?	Rejection Criteria per WSC-07-350[1]	Required Corrective Action	Required Analytical Response Action
Initial Demonstration of Proficiency (IDP)	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 Section 8.6 of SW-846 9010C and the requirements in Section 1.1.2 of this protocol.	No	NA	Refer to Section 8.6 of SW-846 9010C and Section 1.1.2 of this protocol.	NA
Preparation of Samples	Accuracy and Representativeness	(1) For Total Cyanide and PAC, all aqueous and solid samples must be distilled/prepared prior to analysis. See SW-846 9010C, 9013, Standard Method 4500-CN, and MassDEP PAC Protocol (Appendix VI A-4) for appropriate reflux distillation procedures.	No	NA	NA	NA
Initial Calibration	Laboratory Analytical Accuracy	(1) Frequency: Daily prior to sample analysis, when daily calibration QC samples (LLCV, CCV, CCB) are not in control, or when major instrument maintenance is performed. (2) 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. High level standard in calibration defines the upper end of the linear calibration range. (4) Linear regression with correlation coefficient r $\geq$0.995. (5) If titration procedure is used, the silver nitrate solution must be standardized as described in "Standard Methods for the Examination of Water and Wastewater," Method 4500-CN D.	No	NA	Perform instrument maintenance as necessary; recalibrate as required by method.	Suspend all analyses until initial calibration meets criteria.

Table VI A-1: Specific QC Requirements and Performance Standards for Total Cyanide and PAC using WSC-CAM-VI A

Required QC Parameter	Data Quality Objective	Required Performance Standard	Required Deliverable?	Rejection Criteria per WSC-07-350[1]	Required Corrective Action	Required Analytical Response Action
Initial Calibration Verification (ICV)	Laboratory Analytical Accuracy	(1) Frequency – immediately after each initial calibration. (2) Prepared using standard source different than used for initial calibration (un-distilled). (3) Concentration level near midpoint of curve. (4) Percent recovery must be 85-115%.	No	NA	(1) Reanalyze ICV; if acceptable, no further action required. (2) If reanalysis is still outside of criteria, recalibrate and reanalyze ICV.	Suspend all analyses until ICV meets criteria.
Initial Calibration Blank (ICB)	Laboratory Analytical Sensitivity (instrument drift & contamination)	(1) Frequency: Immediately after ICV. (2) Un-distilled. (3) Cyanide must be <RL.	No	NA	(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.
Low-Level Calibration Verification (LLCV)	Laboratory Analytical Sensitivity (verify low-end of calibration range / verify RL)	(1) Frequency: Daily prior to sample analysis if initial calibration is not performed on same day as sample analysis. If initial calibration is performed on same day as sample analysis and includes the RL 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 level must be at the level of the RL for Cyanide. (4) Percent recovery must be 70-130%.	No	NA	(1) Reanalyze LLCV; if acceptable, no further action required. (2) If reanalysis is still outside of criteria and concentrations of Cyanide are ≤10x RL in associated field samples, recalibrate and reanalyze LLCV and associated samples. (3) If concentrations of Cyanide are >10x RL in associated field samples, include explanation in laboratory narrative; no further action required.	Suspend all analyses until LLCV meets criteria unless the concentrations of Cyanide are >10x RL in the associated field samples.
Continuing Calibration Verification (CCV)	Laboratory Analytical Accuracy	(1) Frequency - Every 20 field samples and at the end of the analytical run. (2) Prepared using same source as initial calibration standards: un-distilled. (3) Concentration level near midpoint of curve. (4) Percent recovery must be 85-115%.	No	NA	(1) Reanalyze CCV; if acceptable, no further action required. (2) If reanalysis is still outside of criteria, recalibrate and reanalyze all associated samples	If (3) applies, include explanation in laboratory narrative.

Table VI A-1: Specific QC Requirements and Performance Standards for Total Cyanide and PAC using WSC-CAM-VI A

Required QC Parameter	Data Quality Objective	Required Performance Standard	Required Deliverable?	Rejection Criteria per WSC-07-350[1]	Required Corrective Action	Required Analytical Response Action
					since last compliant CCV – unless (3) applies. (3) If recovery is high (>115%) and all associated sample results are non-detected, no corrective action required.	
Continuing Calibration Blank (CCB)	Laboratory Analytical Sensitivity (instrument drift & contamination)	(1) Frequency - Every 20 field samples following CCV and at the end of the analytical run. (2) Un-distilled. (3) Cyanide must be <RL.	No	NA	(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. (3) If concentration of Cyanide in CCB is >RL but all associated sample results are either non-detected or >10x concentration of Cyanide in CCB, no corrective action required.	If (3) applies, include explanation in laboratory narrative
Method Blank (MB)	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) Cyanide must be <RL.	Yes	NA	(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 Cyanide in MB is >RL but all associated sample results are either non-detected or >10x concentration of Cyanide in MB, no	If (3) applies, include explanation in laboratory narrative.

Table VI A-1: Specific QC Requirements and Performance Standards for Total Cyanide and PAC using WSC-CAM-VI A

Required QC Parameter	Data Quality Objective	Required Performance Standard	Required Deliverable?	Rejection Criteria per WSC-07-350[1]	Required Corrective Action	Required Analytical Response Action
					corrective action required.	
Laboratory Control Sample (LCS) for Total Cyanide and Positive Laboratory Control Sample (LCS-P) for PAC	Laboratory Analytical Accuracy (Method Performance for PAC)	(1) Frequency – One per distillation batch of ≤20 field samples. (2) Total Cyanide: LCS must be matrix-matched by distilling with the samples using the same preparation method. CAM requires a solid Standard Reference Material (SRM) be prepared and analyzed with solid field samples as the "solid LCS." An SRM is a soil or sediment matrix that contains Cyanide at a known concentration and with 95% confidence limits. PAC: LCS-P is always an aqueous matrix but is distilled with both solid and aqueous samples. (3) Total Cyanide: Concentration level for aqueous LCS near midpoint of curve. PAC: Concentration of LCS-P = 0.1 mg/L KCN. (4) LCS and LCS-P must be distilled with samples in batch. (5) Total Cyanide: Percent recovery must be 80-120% for aqueous LCS and within vendor control limits (95% confidence limits) for solid LCS. PAC: Percent recovery must be 80-120%.	Yes	Aqueous LCS or LCS-P: Recovery <50%: Cyanide results in associated samples may be rejected.	(1) Reanalyze LCS: if acceptable, no further action required. (2) If reanalysis is still outside of criteria and LCSD is in-control for cyanide, 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.	Report recovery exceedances in laboratory narrative.
LCS Duplicate for Total Cyanide and LCS-P Duplicate for PAC	Laboratory Analytical Accuracy & Precision	(1) Frequency – One per distillation batch of ≤20 field samples ONLY if not performing project-specific MD. (2) Total Cyanide: LCS Duplicate must be matrix-matched by distilling with the samples using the same preparation method. CAM requires 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 Cyanide at a known concentration and with 95%	Yes	Same as above for LCS for recovery evaluation.	(1) Reanalyze LCSD; if acceptable, no further action required. (2) If reanalysis is still outside of recovery criteria for cyanide, and LCS is in-control for cyanide recovery, no corrective action required. (3) If LCSD and LCS are	Report recovery and RPD exceedances in laboratory narrative.

Table VI A-1: Specific QC Requirements and Performance Standards for Total Cyanide and PAC using WSC-CAM-VI A

Required QC Parameter	Data Quality Objective	Required Performance Standard	Required Deliverable?	Rejection Criteria per WSC-07-350[1]	Required Corrective Action	Required Analytical Response Action
		confidence limits. PAC: LCS-P duplicate is always an aqueous matrix but is distilled with both solid and aqueous samples. (3) Concentration levels must be same as LCS. (4) LCS Duplicate and LCS-P Duplicate must be distilled with samples in batch. (5) Total Cyanide: Percent recovery must be 80-120% for aqueous LCS and within vendor control limits (95% confidence limits) for solid LCS. PAC: Percent recovery must be 80-120%. (6) Analyze immediately after LCS or LCS-P in analytical sequence (7) Total Cyanide: RPDs must be ≤20 for aqueous LCS/LCSD and ≤30 for solid LCS/LCSD. PAC: RPDs must be ≤20 for LCS-P/LCS-P Duplicate.			both outside of recovery criteria, redistill and reanalyze LCS/LCSD and all associated field samples in batch.	
Negative Laboratory Control Sample (LCS-N) for PAC	Method Performance for PAC	(1) Frequency - One per distillation batch of ≤20 field samples. (2) LCS-N must be distilled with samples in batch. (3) Concentration LCS-N = 1.0 mg/L Prussian Blue (Iron-cyanide). (4) Percent recovery must be ≤10 %. (5) LCS-N is always an aqueous matrix but is distilled with both solid and aqueous samples.	Yes	NA	Redistill and reanalyze LCS-N and all associated field samples in batch.	Suspend all analyses until LCS-N meets criteria.
Matrix Spike (MS) Total Cyanide & PAC Project-Specific	Method Accuracy in Sample Matrix	(1) Solid Samples (Soil/Sediment) Frequency: One per 20 field samples per matrix; designated by data user on COC or at project set-up. Aqueous Samples 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) Total Cyanide: Concentration level near	Yes ONLY when requested by the data user	Recovery <30%: affects non-detects for Cyanide in all associated samples.	(1) Reanalyze MS; if acceptable, no further action required. (2) After reanalysis, if MS recovery is 30-74% or >125% and LCS (or LCS-P) was in control, no corrective action is required. (3) If MS recovery is <30%	Report MS exceedances in laboratory narrative. If redigested due to recoveries <30%, report both sets of sample/MSdata.

Table VI A-1: Specific QC Requirements and Performance Standards for Total Cyanide and PAC using WSC-CAM-VI A

Required QC Parameter	Data Quality Objective	Required Performance Standard	Required Deliverable?	Rejection Criteria per WSC-07-350[1]	Required Corrective Action	Required Analytical Response Action
		midpoint of curve. PAC: Concentration level same as LCS-P (KCN). (3) Percent recovery must be 75-125%.			and associated with non-detected results, redistill (homogenize sample well) and reanalyze sample/MS pair. Report results and narrate.	
Matrix Duplicate (MD) Total Cyanide & PAC Project-Specific	Method Precision in Sample Matrix	(1) Frequency: One per distillation batch 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 Cyanide must be ≤20 for aqueous and ≤35 for solids.	Yes ONLY when requested by the data user	NA	Narrate.	Report exceedances in laboratory narrative.
General Reporting Issues	NA	(1) Non-detected values must be reported with the sample-specific RL for Total Cyanide and PAC using all appropriate preparation/dilution factors. (2) The laboratory must only report values ≥ the sample-specific RL. (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 MCP regulatory standards. (5) Results must be reported with 2 or more "significant figures" if ≥RL. If reporting values below the RL, report with 1 or more "significant figures".[2] (6) Refer to Appendix VI A-1 for chain-of-custody requirements regarding preservation, cooler temperature, and holding times.	NA	NA	NA	(1) The performance of dilutions must be documented in the laboratory narrative or on the report form. Unless due to elevated concentrations of Cyanide, reasons for dilutions must be explained in the laboratory narrative. (2) If samples are not preserved properly or are not received with an acceptable cooler temperature, note the non-conformances in the laboratory narrative. (3) If samples are distilled and/or analyzed outside of the holding time, note the

Table VI A-1: Specific QC Requirements and Performance Standards for Total Cyanide and PAC using WSC-CAM-VI A

Required QC Parameter	Data Quality Objective	Required Performance Standard	Required Deliverable?	Rejection Criteria per WSC-07-350[1]	Required Corrective Action	Required Analytical Response Action
						non-conformances in the laboratory narrative. (4) Narrate any additional method non-compliance or sample-specific anomaly.

[1] As per Appendix IV of MassDEP Policy #WSC-07-350, *MCP Representativeness Evaluations and Data Usability Assessments*, September 2007, if these results are observed, data users should consider nondetect results as unusable and detected results as estimated with a significant low bias.

[2] Reporting protocol for "significant figures" is a policy decision included for standardization and consistency for reporting of results and is not a definition of "significant" in the scientific or mathematical sense.

2.0 Data Usability Assessment

Specific guidance applicable to all Class A, B or C RAO Statements, including partial RAOs, for preparation of Representativeness Evaluations and Data Usability Assessments pursuant to 310 CMR 40.1056(2)(k) of the MCP is provided in *MCP Representativeness Evaluations and Data Usability Assessments* (Policy #WSC-07-350). This document provides general information regarding the purpose and content of these required evaluations as a component of and in support of an RAO submittal. The most current version of this document may be found at the following URL: https://www.mass.gov/site-cleanup-regulations-policies-forms-more.

Overall usability of data produced using this CAM protocol should be evaluated for compliance with project-specific data objectives using MassDEP Policy #WSC-07-350, regardless of "Presumptive Certainty" status.

3.0 Reporting Requirements for WSC-CAM-VI A

3.1 General Reporting Requirements for WSC-CAM-VI A

General environmental laboratory reporting requirements for analytical data used in support of assessment and evaluation decisions at MCP disposal sites are presented in WSC-CAM-VII A, Section 2.4. This guidance document provides limited recommendations for field QC, as well as the required content of the laboratory report, which includes:

- Laboratory identification information,
- Analytical results and supporting information,
- Sample- and batch-specific QC information,
- Laboratory Report Certification Statement,
- Copy of the Analytical Protocol Certification Form,
- Laboratory narrative contents, and
- Chain-of-custody form requirements.

3.2 Specific Reporting Requirements for WSC-CAM-VI A

Specific QC requirements and performance standards for WSC-CAM-VI A are presented in Table VI A-1. Specific reporting requirements for WSC-CAM-VI A are summarized below in Table VI A-2 as "Required Analytical Deliverables (**YES**)". These routine reporting requirements must always be included as part of the laboratory deliverable for this method. It should be noted that although certain items are not specified as "Required Analytical Deliverables (**NO**)", these data must be available for review during an audit and may also be requested on a client-specific basis.

Soil and sediment results must be reported on a dry-weight basis. Refer to ASTM Method D2216, Determination of Moisture Content of Soils and Sediments, for more detailed analytical and equipment specifications.

Table VI A-2 Routine Reporting Requirements for WSC-CAM-VI A (Total CN & PAC)

Parameter	Required Analytical Deliverable
Initial Calibration	***NO***
Initial Calibration Verification (ICV)	***NO***
Initial Calibration Blank (ICB)	***NO***
Low-Level Calibration Verification (LLCV)	***NO***
Continuing Calibration Verification (CCV)	***NO***
Continuing Calibration Blank (CCB)	***NO***
Method Blank (MB)	***YES***
Total Cyanide Laboratory Control Sample (LCS)	***YES***
PAC Positive Laboratory Control Sample (LCS-P)	***YES***
PAC Negative Laboratory Control Sample (LCS-N)	***YES***
Total Cyanide LCS Duplicate	***YES***
PAC LCS-P Duplicate	***YES***
Matrix Spike (MS)	***YES*** *(if requested by data user)*
Matrix Duplicate (MD)	***YES*** *(if requested by data user)*
Identification and Quantitation	***NO***
General Reporting Issues	***YES***

3.2.2 Sample Dilution

Under circumstances that sample dilution is required because the concentration of Cyanide exceeds the concentration of the highest calibration standard or due to matrix interference, the RL for Cyanide must be adjusted (increased) in direct proportion to the Dilution Factor (DF).

The revised RL for the diluted sample, RL_d:

$$RL_d = DF \times \text{Lowest Calibration Standard for Cyanide}$$

It should be understood that samples with elevated RLs as a result of a dilution may not be able to satisfy MCP standards/criteria in some cases if the RL_d is greater than the applicable MCP standard or criterion to which the concentration is being compared. All dilutions must be fully documented in the laboratory narrative.

Appendix VI A-1

Sample Collection, Preservation, and Handling Procedures for Total Cyanide and PAC Analyses

Sample preservation, container and analytical holding time specifications for aqueous, soil and sediment matrices for Total Cyanide and PAC analyzed in support of MCP decision-making are summarized below and presented in Appendix VII A-1 of WSC-CAM-VII A, *Quality Assurance and Quality Control Guidelines for the Acquisition and Reporting of Analytical Data Conducted in Support of Response Actions Conducted Under the Massachusetts Contingency Plan (MCP)*. Additional guidance may be found in SW-846, Chapter Three.

Matrix	Container[1]	Preservation[4]	Holding Time[2]
Aqueous	250 mL Polyethylene or Glass bottle for micro-distillation procedure; 1 L Polyethylene or Glass bottle for macro-distillation procedure	Total CN & PAC: NaOH to pH ≥ 12.0; Cool to ≤ 6°C but not frozen; 0.6 g ascorbic acid per liter, if residual chlorine is suspected PAC: Keep out of direct light	14 days to distillation; analyze distillates within 24 hours of distillation
Soil and Sediments	4-ounce glass jar with inert (Teflon) liner	Total CN & PAC: Cool to ≤ 6°C but not frozen PAC: Keep out of direct light	14 days to distillation; analyze distillates within 24 hours of distillation
Waste Samples[3]	250 mL amber wide-mouth jar with inert (Teflon) liner	Total CN & PAC: Cool to ≤ 6°C but not frozen PAC: Keep out of direct light	As soon as possible

[1]The collection of multiple sample containers per sample location may be required to collect enough sample for matrix QC.

[2]Holding time begins from time of sample collection. As per Appendix IV of MassDEP Policy #WSC-07-350, *MCP Representativeness Evaluations and Data Usability Assessments*, September 2007, if the holding time is exceeded by >2x, data users should consider non-detect results as unusable and detected results as estimated (low bias).

[3]Samples containing, or suspected of containing, cyanide or a combination of cyanide and sulfide wastes should be collected with a minimum of aeration. The sample container should be filled completely, excluding all headspace, and capped. Analysis should commence as soon as possible.

[4]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.

Appendix VI A-2

Data Deliverable Requirements for Data Audits

If requested by MassDEP, submission of the information listed below may be required to perform a data audit to verify compliance with the analytical methods and to evaluate accuracy and reliability of the reported results. These deliverables represent a "full data package" including all sample documentation from receipt through preparation, analysis, and data reporting. The laboratory must ensure that these deliverables are available, in the event a data audit is performed. The laboratory is required to retain these deliverables for a period of 10 years from the date generated.

DELIVERABLE REQUIREMENTS FOR DATA AUDITS WSC-CAM-VI A (Total Cyanide and PAC)	
Laboratory Narrative	Must comply with the required laboratory narrative contents as described in WSC-CAM-VII A
Sample Handling Information	Chain-of-custody (external and internal), sample receipt logs (cooler temperatures and sample pH), correspondences
Miscellaneous Logs	Dry weight logs; Analytical logs; Freezer logs
Initial Calibration Data	Raw instrument data for initial calibration, including calculation of linear or non-linear regression and correlation coefficient values; Concentrations of calibration standards used
Initial Calibration Verification and Initial Calibration Blank Data	Percent recoveries for all ICVs; ICV source & true value; Results and raw instrument data for ICV and ICB
Low-Level Calibration Verification, Continuing Calibration Verification, and Continuing Calibration Blank Data	Percent recoveries for all LLCV and CCV; LLCV and CCV source & true value; Results and raw instrument data for LLCV, CCV, and CCB
Sample Results	Sample result forms with dilution factors, units, reporting limits, method reference, date of preparation, date of analysis; Raw instrument data; Percent solids results; Sample preparation/distillation logs (initial and final weights/volumes; preparation method reference)
Method Blank Results	Method Blank results, units, reporting limits; Raw instrument data; Preparation logs
LCS/LCS Duplicate Results (negative and positive LCS for PAC) and/or SRM results	Summary of results, including concentrations detected, concentrations spiked or known (vendor limits) if SRM, percent recoveries and RPDs; Raw instrument data; Preparation logs
MS Results – if analyzed **MD Results – if analyzed**	Summary of results, project-specific sample ID, unspiked sample concentration, concentration detected, concentration spiked, percent recoveries and RPDs; Raw instrument data; Preparation logs

Appendix VI A-3

Analysis Sequence for Total Cyanide and PAC by WSC-CAM-VI A

Typical analytical sequence for Total Cyanide and PAC using WSC-CAM-VI A:

- Initial Calibration
- ICV
- ICB
- LLCV – only required if initial calibration curve not performed on same day as analysis or performed on the same day but does not have a low-level standard at the level of the RL
- MB
- Total CN: LCS / PAC: LCS-P and LCS-N
- Total CN: LCSD / PAC: LCSD-P (LCSD only required if not performing a project-specific MD)
- Total CN: 17 samples – include the project-specific MS and/or MD if applicable / PAC CN: 15 samples – include the project-specific MS and/or MD if applicable
- CCV
- CCB
- 20 samples
- CCV
- CCB
- Etc. (continue 20 samples and CCV/CCB pairs)
- CCV – ending
- CCB – ending

Appendix VI A-4

Method for the Determination of Physiologically Available Cyanide (PAC)

METHOD FOR THE DETERMINATION OF

PHYSIOLOGICALLY AVAILABLE CYANIDE (PAC)

Massachusetts Department of Environmental Protection

Division of Environmental Analysis
(Senator William X. Wall Experiment Station)

Office of Research and Standards

Bureau of Waste Site Cleanup

December 2009
Revision 1
(Replaces the PAC Method published on August 13, 2004)

MassDEP
Physiologically Available Cyanide (PAC) Method

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1.0 PAC Overview

The MassDEP Physiologically Active Cyanide (PAC) Method is a performance based reflux-distillation procedure that is used for the determination of biologically available cyanides and is intended to simulate the interaction of the human digestive system and ingested cyanide complexes. PAC is defined as the quantity of cyanide released during distillation under the temperature and pH conditions specified by this protocol. The cyanide forms released in this distillation include free cyanide, simple cyanide complexes (such as cyanide salts) and certain metal cyanides; with the exception of iron-cyanide complexes (including "Prussian Blue") that are not released under the analytical conditions of this protocol.

Cyanide in the form of hydrocyanic acid (HCN) is released from environmental samples during the PAC distillation under acidic conditions of pH 2 and controlled temperature (to mimic stomach conditions) and captured into an alkaline scrubber solution. The concentration of cyanide in the scrubber solution is then determined spectrophotometrically or titrimetrically by SW-846 Method 9014, SW-846 9012B, or Standard Method 4500-CN-. An additional requirement of both a positive and negative laboratory control sample for PAC is required QC for this method. Analysis by the WSC-CAM-VI A protocol is recommended in support of MCP decisions.

Method performance is verified by the evaluation of the percent recovery of a Positive Laboratory Control Sample (LCS-P) and a Negative Laboratory Control Sample (LCS-N). Potassium Cyanide (KCN) is used as the LCS-P and Prussian Blue is used as the LCS-N for the PAC method. Acceptable percent recovery criteria for LCS-P and LCS-N are listed in Section 7, below and in Table VI A-1 of the WSC-CAM-VI A protocol.

This document details instructions for the manual macro (large-volume) PAC cyanide distillation (macro-distillation) procedure. For alternative micro semi-automatic PAC cyanide distillation (micro-distillation) procedures, follow manufacturer's instructions regarding the adjustment of analytical reagent volumes.

2.0 Sample Preparation

2.1 Soil and Sediment Analysis

Soil and sediment samples are prepared as-received. Pass the soil/sediment sample through a #10 sieve. Discard any material retained on the sieve. Homogenize the sieved sample by stirring with a stainless steel spoon or placing in a mechanical stirring device. Place 10 g of sieved soil/sediment in the reaction flask for the macro-distillation (1 g for the micro-distillation). The PAC concentration in the reaction flask must not exceed 20 mg/L. Perform a percent solids analysis on a separate soil/sediment aliquot. Use the percent solids to report soil/sediment PAC results on a dry-weight basis.

2.2 Aqueous Analysis

Aqueous samples for PAC require no additional preparation prior to distillation. Place 500 mL of the aqueous sample for macro-distillation (50 mL for micro-distillation) directly into the reaction flask. The PAC concentration in the reaction flask must not exceed 20 mg/L. For the macro-distillation, a sample aliquot may be diluted appropriately with distilled water to a final volume of 500 mL to accommodate this requirement.

2.3 Waste Analysis

Solid and oily waste samples should be extracted prior to PAC distillation using SW-846 Method 9013 *Cyanide Extraction Procedure for Solids and Oils*. The waste sample is first extracted with water at pH ≥10. The resultant extract is then distilled using this PAC method, following the aqueous preparation/distillation procedure.

3.0 Reagent Preparation

The following reagent preparation guidelines are for the ***macro-distillation*** procedure. For the micro-*distillation* procedure, adjust reagents according to manufacturer's instructions.

Phosphate Buffer Solution - Dissolve 500 g of $NaH_2PO_4.H_2O$ to 500 mL of distilled water in a one-liter beaker. With the electrode of a pH meter immersed in the solution, adjust the pH of the solution to 1.25 with concentrated phosphoric acid while stirring.

Magnesium Chloride Solution - Dissolve 510 g of $MgCl_2.6H_2O$ in 1-liter of distilled water to prepare a 2.5M $MgCl_2$ solution

Sodium Hydroxide Solution - Dissolve 50 g of NaOH in 1-liter of distilled water to prepare a 1.25N NaOH solution.

Sulfamic Acid (H_2NSO_3H)

Cadmium Carbonate ($CdCO_3$)

4.0 Apparatus and Materials

The required apparatus and materials for the PAC distillation (macro-distillation) are described in Section 4.0, SW-846 Method 9010C, *Total and Amenable Cyanide: Distillation*. Cyanide, as hydrocyanic acid (HCN), is released from samples by acid hydrolysis/distillation and captured in an alkaline mediated gas scrubber under vacuum. Additional requirements are as follows:

- ✓ Samples should be analyzed in a fume hood,
- ✓ A flow meter should be placed at the air inlet, and
- ✓ Equipment should be set-up in a thermostatically-controlled constant temperature bath, or equivalent (such as heating blocks or heating mantles), to maintain constant temperature of distillation. Manual temperature control is less preferable, but allowable if fully documented.

5.0 Sample Distillation

The following distillation procedure is for the ***macro-distillation***. For the micro-distillation, adjust reagents, amounts, and times according to manufacturer's instructions.

5.1 An aliquot of 10.0 ± 1.0 g (w/w) of soil/sediment or 500 mL of aqueous sample (or sample diluted to 500 mL) is placed directly in the 1-liter reaction flask. For soil/sediment samples, rinse the weighing container with distilled water to ensure complete sample transfer and bring to a final analytical volume of 500 mL. Add the distilled water with manual swirling to ensure complete surface contact.

5.2 Add 50 mL of the sodium hydroxide solution (1.25N). Connect the reaction flask, condenser, gas scrubber and vacuum trap. If high sulfides are expected in the sample, add 10 to 15 mg of $CdCO_3$ to the trap. Set temperature of thermostatically controlled constant temperature bath to 78 ± 3°C. When bath has equilibrated at 78°C, place the reaction flask in the bath and apply vacuum to initiate gas flow through gas scrubber.

5.3 Add 75 mL of the phosphate buffer solution, 2 g of sulfamic acid (H_2NSO_3H), and 20 mL of $MgCl_2$ solution through the inlet tube. Test the pH of the solution in the reaction flask to verify that the pH ≤ 2. Place the thermometer in the inlet tube to record the temperature of the solution in the reaction flask.
Note: If using the micro-distillation procedure, pH cannot be checked until the reaction is complete as the micro-distillation apparatus is a closed-system.

5.4 Record the reaction flask temperature every 15 minutes. Maintain the temperature at 78 ± 3^{o} C for a period of **one hour**. Record total reaction time (the total time that the flask is in the water bath). Airflow should be measured at least every 15 minutes. Adjust the vacuum rate so that approximately two bubbles of air per second enter the flask through the air inlet tube (this is the same flow requirement as for total Cyanide by SW-846 Method 9010C). This will translate to a flow rate of 290 to 350 ml/min, depending upon laboratory equipment used, and should be maintained for the total one-hour reaction time. Care should be taken that the sodium hydroxide solution in the gas scrubber does not bubble over.

5.5 After the one hour of reaction time, turn off heating source and allow sample to come to room temperature. Measure the pH of the solution in the reaction flask electrochemically (probe) to verify that the pH was maintained at ≤ 2 during the reaction. Test the absorber solution with lead acetate paper for the presence of excess sulfide before analysis. Treat with bismuth nitrate, as necessary (see SW-846 Method 9010C Section 7.2 for details on treatment of distillates for sulfide).

Analytical Note: The analyst must be continually aware of the potential for cross-contamination. Measured PAC concentrations are generally at or near the method reporting limit. As such, the method is particularly susceptible to positive interferences from the presence of low level cyanide residues on glassware from previous analyses of samples and/or various QC samples and standards with elevated PAC concentrations. Thus, frits, absorber tubes, and condensers should be cleaned with dilute HCl and then rinsed with distilled water between samples.

6.0 Analysis

For the macro-distillation procedure, the entire content of the absorber tube is transferred to a 250 mL volumetric flask. The tube is rinsed with distilled water, with the rinsate added to the flask. The absorbing solution is then brought to volume with distilled water.

The following determinative methods may be used for analysis of PAC in distillates:

- SW-846 Method 9014 – manual colorimetric UV spectrometry for the determination of free (non-complexed) Cyanide (CN^-) and hydrocyanic acid (HCN) in solution/distillates.
  - This method also includes titrimetric determination; however, the sensitivity of the titrimetric method may not meet data quality objectives (see Section 1.6 of the WSC-CAM-VI A protocol for further information)
- SW-846 Method 9012B – 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

For colorimetric methods, the distillate is treated with chloramine-T at pH <8 to convert the HCN into cyanogen chloride (CNCl) and color is formed by adding pyridine-barbituric acid. Quantitation for PAC in the treated distillates is based on the color absorption at 578-nm wavelength using a UV spectrometer. Absorbance (peak height) is measured as a function of PAC concentration, based on a multi-level calibration curve.

Analysis by WSC-CAM-VI A protocol is recommended in support of MCP decisions.

7.0 Quality Control

Required quality control (QC), frequency, and acceptance criteria for PAC can be found in WSC-CAM-VI A, Table VI A-1 Specific QC Requirements and Performance Standards for Total Cyanide and PAC using WSC-CAM-VIA. Some of the required QC parameters are highlighted below:

One method blank (MB) sample must be distilled with each PAC batch of up to 20 samples. The PAC result must be less than the RL.

Accuracy of the PAC method is measured by two required LCS, which must be distilled with each PAC batch of up to 20 samples:

- Positive Laboratory Control Sample (LCS-P) = 0.1 mg/L Potassium Cyanide (KCN) standard. LCS-P percent recovery (%R) must be 80-120%R of the true value (0.1 mg/L).
- Negative Laboratory Control Sample (LCS-N) = 1.0 mg/L Prussian Blue (iron-cyanide) standard. LCS-N percent recovery must be $\leq$10% of the true value (1.0 mg/L).

In addition to the LCS-P and LCS-N, a project-specific Matrix Spike (MS) is required for PAC in solid matrices (soil/sediment) for WSC-CAM-VI A compliance. For PAC, the spiking solution used for the MS is the LCS-P (KCN standard) and the recovery must be 75-125%.

See the WSC-CAM-VI A protocol, Table VI A-1 for additional details on PAC performance standards and required corrective actions.

8.0 Method Performance Criteria

Compliance with the LCS-P, LCS-N, and MS QC requirements described in Section 7.0 above and Table VI A-1 of the WSC-CAM-VI A protocol is the basis for evaluation of satisfactory PAC performance. Conformity with the PAC method temperature and flow rate specifications in Section 4, together with other specific analytical specifications, is expected under most circumstances to produce acceptable PAC QC results. However, it is expected that some laboratories will be able to satisfy PAC QC requirements even with modifications of this method's temperature and flow rate specifications. For example, one laboratory that assisted MassDEP in method development was able to achieve acceptable recoveries for both LCS-P and LCS-N QC standards for samples distilled at 72^{o}C with a flow rate of 325-350 mL/min.

9.0 Sample Collection, Preservation, and Holding Time Specifications

Sample preservation, container and analytical holding time specifications for surface water, groundwater, soil/sediment and waste samples for PAC analyses conducted in support of MCP decision-making are described in Appendix VI A-1 of the WSC-CAM-VI A protocol.

Figure 1 PAC Preparation/Distillation Flow Chart