WSC – CAM – VI B

Quality Control Requirements and Performance Standards for the **Analysis of Hexavalent Chromium, Cr(VI), by UV-Visible Spectrophotometry or Ion Chromatography** in Support of Response Actions under the Massachusetts Contingency Plan (MCP)

VI. Miscellaneous Wet Chemical Methods

B. Quality Control Requirements and Performance Standards for WSC-CAM-VI B (Hexavalent Chromium)

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ACRONYM LIST

CAM	Compendium of Analytical Methods
CASN	Chemical Abstracts Service Number
CCB	Continuing calibration blank
CCV	Continuing calibration verification
COC	Chain-of-custody
Cr(III)	Trivalent Chromium
Cr(VI)	Hexavalent Chromium
DF	Dilution factor
ICB	Initial calibration blank
ICV	Initial calibration verification
LCS/LCSD	Laboratory control sample / Laboratory control sample duplicate
LLCV	Low-level calibration verification
LLOQ	Lower limit of quantitation
MassDEP	Massachusetts Department of Environmental Protection
MB	Method blank
MCP	Massachusetts Contingency Plan
MD	Matrix duplicate
MOHML	Massachusetts Oil and Hazardous Materials List
MS	Matrix spike
MSD	Matrix spike duplicate
ORP	Oxidation/Reduction Potential
PDS	Post-digestion Spike
QA	Quality assurance
QC	Quality control
r	Correlation coefficient
RCs	Reportable Concentrations
RL	Reporting limit
RPD	Relative percent difference
RQs	Reportable Quantities
SRM	Standard reference material
USEPA	United States Environmental Protection Agency

<u>UNITS</u>:

mg/kg	Milligram per kilogram
mL	Milliliter
µg/L	Microgram per liter
µm	Micron

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

1.1 Overview of WSC-CAM-VI B

WSC-CAM-VI B, *Quality Control Requirements and Performance Standards for the Analysis of Hexavalent Chromium, Cr(VI), by UV-Visible Spectrophotometry or Ion Chromatography in Support of Response Actions under the Massachusetts Contingency Plan (MCP)*, is a component of MassDEP's Compendium of Analytical Methods (CAM). Effective October 15, 2024, this revised CAM protocol, WSC-CAM-VI B, replaces the previous version of the Hexavalent Chromium CAM document, WSC-CAM-VI B (effective date, July 1, 2010). 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 October 15, 2024 for the purpose of "Presumptive Certainty," the revised protocol may be used optionally prior to its effective date upon its publication on July 15, 2024.

This document provides Quality Control (QC) requirements and performance standards to be used in conjunction with the required analytical methods SW-846 7196A (or the most current version) or SW-846 7199 (or the most current version), analysis for Hexavalent Chromium (Cr(VI)) in aqueous and solid samples using UV-Visible spectrophotometry or ion chromatography, respectively, preceded by sample preparation for solid samples, as described in Section 1.3 of this protocol. The QC requirements and performance standards specified in this document in Table VI B-1 together with the analytical procedures described in EPA SW-846 Method 7196A, *Chromium, Hexavalent (Colorimetric)*, or EPA SW-846 Method 7199, *Determination of Hexavalent Chromium in Drinking Water, Groundwater and Industrial Wastewater Effluents by Ion Chromatography*, constitute the WSC-CAM-VI B 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 7196A or EPA SW-846 7199 is a "Presumptive Certainty" requirement of WSC-CAM-VI B.

Sample preservation, container and analytical holding time specifications for aqueous, soil, and sediment matrices for Hexavalent Chromium analyzed in support of MCP decision-making are presented in Appendix VI B-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 or Lower Limits of Quantitation for Hexavalent Chromium by WSC-CAM-VI B

The reporting limit (RL) or lower limit of quantitation (LLOQ) for Hexavalent Chromium (Cr(VI)) using WSC-CAM-VI B 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/LLOQs for Cr(VI) using the WSC-CAM-VI B protocol are:

- 5 – 10 µg/L for aqueous samples (surface water, groundwater, and drinking water) using SW-846 Method 7196A;
- 1 – 10 µg/L for aqueous samples (surface water, groundwater, and drinking water) using SW-846 Method 7199; and
- 0.5 – 1.0 mg/kg for soil/sediment samples (assuming 100% solids).

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

RLs/LLOQs lower than the above-referenced CAM RLs/LLOQs for Cr(VI) may be required to satisfy project requirements. The RL/LLOQ (based on the concentration of the lowest calibration standard or the LLCV) for Cr(VI) 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. RLs/LLOQs for Cr(VI) will be proportionately higher for samples that require dilution, when a reduced sample size is used, or when the sample has a relatively high percent moisture (low percent solids).

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

Each laboratory that uses the WSC-CAM-VI B protocol is required to operate a formal quality assurance (QA) 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 digestion/analysis of laboratory control samples (LCS) and LCS duplicates (LCSD) to assess accuracy and precision. Matrix spikes (MS), matrix spike duplicates (MSD), or matrix duplicates (MD) may also be used to evaluate accuracy and/or precision when such samples are analyzed either at the discretion of the laboratory or at the request of the data user.

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 B-1 of this protocol. 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 B must include the following information:

QC Element	**Performance Criteria**
Initial Calibration	WSC-CAM-VI B, Table VI B-1
Continuing Calibration Verification	
Method Blanks	
Percent Recovery for LCS & MS Solids: Soluble MS & Insoluble MS recoveries	
Relative Percent Difference (RPD) for LCSD or MD	

Laboratories are encouraged to actively monitor pertinent QC performance standards described in Table VI B-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 B protocol, laboratory-specific control limits must meet or exceed (demonstrate less variability than) the performance standards for each QC element listed in Table VI B-1. It should be noted that the performance standards listed in Table VI B-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 experienced in the use of colorimetric UV-Visible spectrophotometry or ion chromatography as a quantitative tool for environmental analyses and knowledgeable in the minimization of interferences described in these methods.

1.2 Summary of SW-846 Methods 7196A and 7199

SW-846 Method 7196A is used to determine Cr(VI) by UV-Visible spectrophotometry in solution. This method may be used directly for the determination of dissolved Cr(VI) in aqueous environmental samples (groundwaters and surface waters) and in extracts or as the determinative step in the analysis of Cr(VI) in soils, sediments and other solid waste materials that have been digested (prepared) using SW-846 Method 3060A, *Alkaline Digestion for Hexavalent Chromium*.

SW-846 Method 7199 is used to determine dissolved Cr(VI) by ion chromatography directly in aqueous environmental samples (drinking water, groundwater, surface water).

Three types of chromium may be of interest in environmental samples: Total Chromium, Cr(VI), and trivalent chromium (Cr(III)). Total Chromium may be determined by inductively coupled plasma-optical emission spectrometry, graphite furnace atomic absorption, or inductively coupled plasma-mass spectrometry. Refer to the appropriate MassDEP CAM protocols (WSC-CAM-III A, III C or III D, respectively) for specific analytical and reporting requirements. Cr(III) is not measured directly; rather, it is defined as the difference between the Total Chromium and the Cr(VI) concentrations, as follows:

$$\text{Chromium (III)} = \text{Total Chromium} - \text{Chromium (VI)}$$

In SW-846 Method 7196A, Cr(VI) is determined by the addition of an excess of diphenylcarbazide in acid solution yielding a red-violet product in the treated sample. Quantitation for Cr(VI) in the treated dissolved or digested sample is based on the color absorption of this red-violet product at 540-nm wavelength using a UV-Visible spectrophotometer. Absorbance (peak height) is measured as a function of Cr(VI) concentration, based on a multi-level calibration curve.

In SW-846 Method 7199, a measured volume of pH-adjusted sample is injected into the ion chromatograph. Organics are removed via a guard column and the Cr(VI), as the chromate ion CrO_4^{2-}, is separated on an anion exchange separator column. Post-column derivatization of the Cr(VI) with diphenylcarbazide is then followed by detection via ion chromatography at an absorbance of 530 nm. Absorbance (peak height or area) is measured as a function of Cr(VI) concentration, based on a multi-level calibration curve.

1.3 Sample Digestion/Preparation Methods for WSC-CAM-VI B

Aqueous samples for analysis by WSC-CAM-VI B do not require preparation/digestion prior to analysis. Solid samples (soil, sediment, sludge, waste) for analysis by WSC-CAM-VI B must be prepared/digested using SW-846 Method 3060A, which is an alkaline digestion procedure for extracting Cr(VI) from solid samples. Alkaline digestion is the required preparative step for the analysis of soils, sediments, sludges and similar waste materials under the WSC-CAM-VI B protocol.

To accurately measure all forms of Cr(VI) in a solid matrix, three criteria must be satisfied:

(1) The digestion solution must solubilize all forms of Cr(VI),
(2) The conditions of the digestion must not cause reduction of native Cr(VI) to Cr(III), which can cause a low bias, and
(3) The conditions of the digestion must not cause oxidation of native Cr(III) to Cr(VI), which can cause a high bias.

SW-846 Method 3060A meets these criteria for most solid matrices. Under the alkaline conditions of the digestion, minimal reduction of Cr(VI) or oxidation of native Cr(III) occurs. The efficiency (measured as percent recovery) of the extraction procedure is assessed using MS recovery data for soluble (potassium chromate) and insoluble (lead chromate) forms of Cr(VI), coupled with the measurement of other soil properties, such as oxidation reduction potential (ORP by measurement of Eh) and pH. See Section 1.6 for further details on these measurements.

Recovery of the insoluble Cr(VI) spike is used to assess efficiency and maintenance of non-reductive conditions during the digestion process. Method-induced oxidation (Cr(III) converted to Cr(VI)) is usually not observed except in soils high in manganese and amended with soluble Cr(III) salts or freshly precipitated $Cr(OH)_3$.

1.4 Method Interferences

Samples submitted to a laboratory for Cr(VI) analysis may become contaminated by numerous routes during both sampling and analysis. Potential sources of contamination may include:

- Metallic or metal-containing containers and sampling equipment,
- Laboratory acids or reagents,
- Improperly cleaned or stored equipment, and

- Atmospheric inputs such as dirt and dust.

Several common interferences and corrective measures are described, as follows.

- SW-846 Method 7196A: The color reaction of Cr(VI) with diphenylcarbazide is highly selective for Cr(VI) and generally free from interferences. Refer to Section 3.0 of SW-846 Method 7196A for further information on analytical interferences, which explains that even relatively high concentrations of potential interferents (molybdenum, mercury salts, iron, vanadium) do not cause a problem with Cr(VI) analysis if performed as specified by SW-846 Method 7196A.
- SW-846 Method 7199: High concentrations of chloride and sulfate can overload the column capacity and cause a loss of Cr(VI). Poor recoveries of Cr(VI) from spiked samples and tailing peaks may be evidence of column overload. Refer to Section 3.0 of SW-846 Method 7199 for further information on analytical interferences.
- SW-846 Method 7199: High concentrations of organics or sulfides may cause reduction of soluble Cr(VI) to Cr(III). Preservation of the sample at a pH of 9-9.5 mitigates this interference, as the predominant species in solution is the chromate ion (CrO_4^{2-}), which is less reactive than the hydrogen chromate ion ($HCrO_4^-$).
- Results for Cr(VI) for soils or wastes that contain levels of soluble Cr(III) greater than 4x the RL/LLOQ for Cr(VI) may be biased high due to method-induced oxidation that can occur during the alkaline digestion (SW-846 Method 3060A) The addition of Mg^{+2} in a phosphate buffer to the alkaline solution has been shown to suppress oxidation. Refer to Section 3.3 of SW-846 Method 3060A.

1.5 Quality Control Requirements and Performance Standards for WSC-CAM-VI B

Specific QC requirements and performance standards for Hexavalent Chromium using the WSC-CAM-VI B protocol are presented in Table VI B-1. Refer to WSC-CAM-VII A for field QC requirements. ***Note that a project-specific matrix spike (MS) must be performed for hexavalent chromium 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) and 40.1057(2)(k) for Permanent and Temporary Solution submittals, respectively, 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 B

The following bullets highlight potential issues that may be encountered with the analysis of Cr(VI) using this protocol.

- Matrix Spike (MS) Recovery – ***A MS is required for WSC-CAM-VI B for hexavalent chromium in solid matrices (soil/sediment) at a frequency of one per 20 samples per matrix***. **Both a Soluble-MS and Insoluble-MS are required to be performed on a project-specific basis for Cr(VI) in solid matrices.** Consistent with the United States Environmental Protection Agency (USEPA) Region I data validation guidance, MassDEP requires rejection of non-detected inorganic results with <30% recovery in the MS if the concentration of Cr(VI) in the unspiked sample is <4x the amount spiked. An exception to this rejection rule applies for solid samples that also demonstrate reducing conditions, as described below for the pH and ORP measurements. If the MS recovery is <30% and non-detected results were reported for Cr(VI), the laboratory must follow the required corrective actions listed on Table VI B-1.
  - Laboratories are not required to monitor whether or not MSs 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.

- When both Total Chromium and Cr(VI) are to be measured in a solid sample, separate sample containers must be collected for each parameter, such that the integrity of the sample for Cr(VI) is maintained prior to digestion (i.e., sample jar not opened prior to alkaline digestion). Therefore, the analysis of pH and ORP cannot be performed on a sample from the container used for Cr(VI), unless these analyses are performed after the aliquot for Cr(VI) has been removed from the container.

- Determinative methods that utilize automated flow injection analysis systems manufactured by Lachat, Technicon and OI Corporation, etc. that use diphenylcarbazide as the color development reagent and maintain the ratio of reagent and sample volumes specified by SW-846 Method 7196A to accommodate automation are considered equivalent for the analysis of dissolved hexavalent chromium both in aqueous environmental samples and the alkaline digestate produced by SW-846 Method 3060A. Manufacturer’s instructions should be consulted for a more detailed discussion of potential method-specific interferences and operational issues. The QC requirements and performance standards described in Table VI B-1 may be applied directly to these methods.

- During sample digestion using SW-846 Method 3060A, the pH must be maintained at pH 7.5 ± 0.5 in order to maintain the native chromium species in the sample (i.e., prevent reduction/oxidation to another species) and to obtain a valid extract for analysis by WSC-CAM-VI B using SW-846 Method 7196A. Failure to meet the pH specifications of the method requires re-digestion of the samples. See Section 7.7 of SW-846 Method 3060A for further information.

- Oxidizing/Reducing Conditions in Sample Matrix – For compliance with WSC-CAM-VI B, determination of the reducing/oxidizing tendency of each soil type and/or sediment matrix for each analytical batch is required when measuring Cr(VI). This is accomplished by characterization of each sample for two additional analytical parameters: pH and ORP. It should be noted that the analysis of pH and ORP must be performed upon receipt at the laboratory (within 24 hours of collection) or in the field during sample collection. Analysis of these parameters can establish the tendency of Cr(VI) to exist or not exist in the unspiked sample(s) and assists in the interpretation of QC data for MS recoveries that are outside of the acceptance criteria. Methods for these additional parameters are as follows:
    - pH by SW-846 Method 9045D for preparation of soil/sediment slurry and then analysis via pH probe measurement directly in the soil/sediment slurry, and
    - ORP (Eh) using SW-846 Method 9045D for preparation of soil/sediment slurry and then analysis via Eh (probe) measurement directly in the soil/sediment slurry using ASTM Method D1498-08.

  Evaluation of Eh-pH should be performed as described in Section 8.5 of SW-846 Method 3060A, using the information presented in Appendix VI B-4 (Eh/pH Phase Diagram) of this WSC-CAM-VI B protocol. Additional information on evaluation of Cr(VI) soluble-MS and insoluble-MS recoveries in solid matrices can be found in the *Quality Control Flow Chart* included as Figure 1 in SW-846 Method 3060A.

  Other direct and indirect indicators of reducing/oxidizing tendency that may be useful in characterizing the soil/sediment and in interpretation of MS recovery results that are outside of acceptance limits include:

    - Ferrous iron
    - Sulfides
    - Total Organic Carbon
    - Chemical Oxygen Demand
    - Biological Oxygen Demand

1.7 Analyte List for WSC-CAM-VI B

The MCP analyte list for WSC-CAM-VI B consists of Hexavalent Chromium (also known as Chromium(VI), Cr(VI), or Cr^{+6}), Chemical Abstracts Service Number (CASN) 18540-29-9, as measured directly in aqueous samples or in alkaline digestates.

It is the responsibility of the data user, in concert with the laboratory, to establish the range and required RL/LLOQ for Cr(VI). Sources of various MassDEP standards and criteria are as follows:

- Reportable Quantities (RQs) and Reportable 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: http://www.mass.gov/dep/cleanup/laws/regulati.htm#mcp
- An online searchable Oil & Hazardous Materials List of RQs and RCs values may be found at the following URL: http://eeaonline.eea.state.ma.us/DEP/MOMHL/hazmat.aspx
- An updated list of MCP Method 1 Standards may be found at the following URL: https://www.mass.gov/regulations/310-CMR-4000-massachusetts-contingency-plan

Cr(VI) has promulgated MCP Method 1 groundwater/soil standards.

Table VI B-1: Specific QC Requirements and Performance Standards for Hexavalent Chromium using WSC-CAM-VI B

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	Laboratory Analytical Accuracy & Precision	(1) Must be performed prior to using method on samples. (2) Must be performed for each matrix. (3) Must follow requirements in Section 1.1.2 of this protocol.	No	NA	Refer to Section 1.1.2 of this protocol.	NA
Preparation of Samples & Additional Measurements	Accuracy and Representativeness	(1) For Cr(VI) in solid samples: must be pretreated/digested prior to analysis. See SW-846 7196A, 3060A, and Section 1.3 of this CAM protocol for appropriate preparation procedures. Note: pH of alkaline digestates of solid samples must be maintained at 7.5 ± 0.5. Follow requirements in Section 7.7 of SW-846 3060A. (2) Additional measurements of pH and ORP (Eh) are required for soil/sediment samples. See Section 1.6 of this CAM protocol for further details.	No	NA	NA	NA
Initial Calibration	Laboratory Analytical Accuracy	(1) 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) Minimum calibration blank plus 5 calibration standards (multi-point); high level standard in calibration defines the upper end of the linear calibration range. (3) Low-level standard in calibration must be at or below the RL/LLOQ. (4) Linear regression with correlation coefficient (r) ≥0.995.	No	NA	Perform instrument maintenance as necessary; recalibrate as required by method.	Suspend all analyses until initial calibration meets criteria.
Initial Calibration Verification (ICV)	Laboratory Analytical Accuracy	(1) Immediately after each initial calibration. (2) Prepared using standard source different than used for initial calibration: undigested. (3) Concentration level near midpoint of curve. (4) SW-846 7196A: Percent recovery must be between 85-115%. (5) SW-846 7199 (referred to as Quality Control Sample): Percent recovery must be between 90-110%.	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.

Table VI B-1: Specific QC Requirements and Performance Standards for Hexavalent Chromium using WSC-CAM-VI B

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 Blank (ICB)	Laboratory Analytical Sensitivity (instrument drift & contamination)	(1) Immediately after ICV. (2) Undigested. (3) Cr(VI) must be <RL/LLOQ.	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/LLOQ)	(1) 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/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: undigested. (3) Concentration level must be at the level of the RL/LLOQ for Cr(VI). (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 Cr(VI) are ≤10x RL/LLOQ in associated field samples, recalibrate and reanalyze LLCV and associated samples. (3) If concentrations of Cr(VI) are >10x RL/LLOQ in associated field samples, include explanation in laboratory narrative; no further action required.	Suspend all analyses until LLCV meets criteria unless the concentrations of Cr(VI) are >10x RL/LLOQ in the associated field samples.
Continuing Calibration Verification (CCV)	Laboratory Analytical Accuracy	(1) SW-846 7196A: Every 15 field samples and at the end of the analytical run. (2) SW-846 7199: Every 10 field samples and at the end of the analytical run. (3) Prepared using same source as initial calibration standards: undigested. (4) Concentration level near midpoint of curve. (5) SW-846 7196A: Percent recovery must be 85-115%. (6) SW-846 7199: Percent recovery must be 90-110%.	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 since last compliant CCV – unless (3) applies. (3) If recovery is high and all associated sample results are not detected, no corrective action required.	If (3) applies, include explanation in laboratory narrative.
Continuing Calibration Blank (CCB)	Laboratory Analytical Sensitivity (instrument	(1) Every 15 field samples (SW-846 7196A) or every 10 samples (SW-846 7199) following CCV and at	No	NA	(1) Reanalyze CCB; if acceptable, no further	If (3) applies, include explanation in laboratory

Table VI B-1: Specific QC Requirements and Performance Standards for Hexavalent Chromium using WSC-CAM-VI B

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
	drift & contamination)	the end of the analytical run. (2) Un-digested. (3) Cr(VI) must be <RL/LLOQ.			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 Cr(VI) in CCB is >RL/LLOQ but all associated sample results are either non-detected or >10x concentration of Cr(VI) in CCB level, no corrective action required.	narrative.
Method Blank (MB)	Laboratory Method Sensitivity (contamination evaluation)	(1) One per analytical or digestion batch of ≤20 field samples. (2) Must be prepared/digested with the samples using the same preparation method as the samples. (3) Cr(VI) must be <RL/LLOQ.	Yes	NA	(1) Reanalyze MB; if acceptable, no further action required. (2) If reanalysis is still outside of criteria, redigest and reanalyze MB and all associated field samples in batch – unless (3) applies. (3) If concentration of Cr(VI) in MB is >RL/LLOQ but all associated sample results are either not detected or >10x concentration of Cr(VI) in MB, no corrective action required.	If (3) applies, include explanation in laboratory narrative.
Laboratory Control Sample (LCS)	Laboratory Analytical Accuracy	(1) One per analytical or digestion batch of ≤20 field samples. (2) Must be matrix-matched by digesting with the samples using the same preparation method. CAM requires a 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 hexavalent chromium at a known concentration and with 95% confidence limits. (3) Concentration level for aqueous LCS near midpoint of curve.	Yes	Aqueous LCS: Recovery <50%: Cr(VI) 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 Cr(VI), no corrective action required. (3) If LCS and LCSD are both outside of criteria, re-digest and reanalyze LCS/LCSD and all	Report recovery exceedances in laboratory narrative.

Table VI B-1: Specific QC Requirements and Performance Standards for Hexavalent Chromium using WSC-CAM-VI B

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
		(4) Percent recovery for Cr(VI) must be 80- 120% for aqueous LCS and within vendor control limits (95% confidence limits) for solid LCS.			associated field samples in batch.	
LCS Duplicate (LCSD)	Laboratory Analytical Accuracy & Precision	(1) One per analytical or digestion batch of ≤20 field samples ONLY if not performing project-specific MD. (2) Must be matrix-matched by digesting with the samples using the same preparation method. CAM requires a solid SRM be prepared and analyzed with solid field samples as the "solid LCSD." An SRM is a soil or sediment matrix that contains hexavalent chromium at a known concentration and with 95% confidence limits. (3) Concentration level must be same as LCS. Analyze immediately following LCS. (4) Percent recovery for Cr(VI) must be 80-120% for aqueous LCS and within vendor control limits (95% confidence limits) for solid LCS. (5) RPDs must be ≤20 for aqueous LCS/LCSD and ≤30 for solid LCS/LCSD.	Yes ONLY if no MD	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 Cr(VI) and LCS is in-control for Cr(VI), no corrective action required. (3) If LCSD and LCS are both outside of recovery criteria, re-digest and reanalyze LCS/LCSD and all associated field samples in batch.	Report recovery and RPD exceedances in laboratory narrative.
Matrix Spike (MS) *Aqueous Samples Only* Project-Specific	Method Accuracy in Sample Matrix	(1) One per digestion batch of ≤20 field samples per matrix is strongly recommended (designated by data user on chain-of-custody [COC] or at project set-up). (2) Concentration level near midpoint of curve. (3) Percent recovery for Cr(VI) must be 85-115%.	Yes ONLY when requested by the data user	Recovery <30%: affects non-detects for Cr(VI) in all associated samples.	(1) Reanalyze MS; if acceptable, no further action required. (2) SW-846 7196A: After reanalysis, if MS recovery is >115% and LCS was in control, no corrective action is required. (3) SW-846 7199A: After reanalysis, if MS recovery ≥30% or >115% and LCS was in control, no corrective action is required. (4) SW-846 7196A: Perform corrective action as per Section 7.4 of SW-846 7196A (making aliquot of extract alkaline, re-spiking, and analyzing). If 85-115%, no further corrective action	Report MS exceedances in laboratory narrative If redigested due to recoveries <30%, report both sets of sample/MS data.

Table VI B-1: Specific QC Requirements and Performance Standards for Hexavalent Chromium using WSC-CAM-VI B

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
					needed (5) If MS recovery is <30% and associated with non-detected results, re-digest and reanalyze sample/MS pair. Report results and narrate.	
Matrix Duplicate (MD) Project-Specific	Method Precision in Sample Matrix	(1) One per digestion batch of ≤20 field samples per matrix is strongly recommended (designated by data user on COC or at project set-up). (2) Prepare by digesting and analyzing an additional aliquot of the same field sample used for MS. (3) RPD for Cr(VI) must be ≤20 for aqueous and ≤35 for solids.	Yes ONLY when requested by the data user	NA	Narrate.	Report exceedances in laboratory narrative.
Soluble Matrix Spike (MS) *Solid Samples Only* Project-Specific	Method Accuracy in Sample Matrix	(1) One per 20 field samples per matrix; designated by data user on COC or at project set-up. (2) Soluble spike = Potassium Chromate ($K_2Cr_2O_7$). (3) Percent recovery of Cr(VI) must be 75-125%.	Yes ONLY when requested by the data user	Recovery <30%; affects non-detects for Cr(VI) in all associated samples. **Exception**: Low recovery of Cr(VI) in soil/sediment may be acceptable if supported by pH and ORP data that demonstrate reducing conditions.	Evaluate LCS. If LCS within acceptance limits, evaluate pH/Eh of sample using figure in Appendix VI B-4. Alternatively, perform mass balance as per Section 8.5.2 of SW-846 3060A. If reducing conditions exist, no further action required. If reducing conditions do not exist: (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 is required. (3) If MS recovery is <30% and associated with non-detected results, re-digest (homogenize sample well) and reanalyze sample/MS	Report MS exceedances in laboratory narrative and note oxidation/reduction characteristics of sample. If redigested due to recoveries <30%, report both sets of sample/MS data.

Table VI B-1: Specific QC Requirements and Performance Standards for Hexavalent Chromium using WSC-CAM-VI B

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
					pair. Report results and narrate.	
Insoluble Matrix Spike (MS) *Solid Samples Only* Project-Specific	Method Accuracy in Sample Matrix	(1) One per 20 field samples per matrix; designated by data user on COC or at project set-up. (2) Insoluble spike = Lead Chromate ($PbCrO_4$). (3) Percent recovery of Cr(VI) must be 75-125%.	Yes ONLY when requested by the data user	Recovery <30%; affects non-detects for Cr(VI) in all associated samples. **Exception**: Low recovery of Cr(VI) in soil/sediment may be acceptable if supported by pH and ORP data that demonstrate reducing conditions.	Evaluate LCS. If LCS within acceptance limits, evaluate pH/Eh of sample using figure in Appendix VI B-4. Alternatively, perform mass balance as per Section 8.5.2 of SW-846 3060A. If reducing conditions exist, no further action required. If reducing conditions do not exist: (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 is required. (3) If MS recovery is <30% and associated with non-detected results, re-digest (homogenize sample well) and reanalyze sample/MS pair. Report results and narrate.	Report MS exceedances in laboratory narrative and note oxidation/reduction characteristics of sample. If redigested due to recoveries <30%, report both sets of sample/MS data.

Table VI B-1: Specific QC Requirements and Performance Standards for Hexavalent Chromium using WSC-CAM-VI B

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
Post-digestion Spike (PDS) *Solid Samples Only* Project-Specific	Method Accuracy in Sample Matrix	(1) One per 20 field samples per matrix. (2) Percent recoveries must be 85-115%.	Yes ONLY if project-specific MS outside acceptance limits	Recovery <30%: affects non-detects for Cr(VI) in all associated samples. Only use PDS in evaluation of analyte in sample data when the same analyte in the MS/MSD fails.	Narrate.	Report exceedances in laboratory narrative.
Duplicate Injections (SW-846 7199 only)	Method Precision in Sample Matrix	(1) Each sample must be injected twice. (2) RPD for Cr(VI) must be ≤20.	NA	NA	Narrate.	Report exceedances in laboratory narrative.
General Reporting Issues	NA	(1) Measurements of ORP (as Eh) and pH must be performed and reported for each solid matrix type. (2) Non-detected values must be reported with the sample-specific RL/LLOQ for Cr(VI) using all appropriate preparation/dilution factors. (3) The laboratory must only report values ≥ the sample-specific RL/LLOQ. (4) Sample concentrations that exceed the highest calibration standard must be diluted and reanalyzed to fall within the linear calibration range. (5) Results for soils/sediments must be reported on a dry-weight basis for comparison to MCP regulatory standards. (6) For aqueous samples, the laboratory must note whether the results are "total" or "dissolved" in the laboratory narrative or on the report form. In addition, if "dissolved", the laboratory must note whether the samples were filtered in the field or at the laboratory. (7) Results must be reported with 2 or more "significant figures" if ≥ RL/LLOQ. If reporting values below the RL/LLOQ, report with 1 or more "significant figures".[2] (8) Refer to Appendix VI B-1 for COC 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 Cr(VI), 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 digested and/or analyzed outside of the holding time, note the non-conformances in the laboratory narrative. (4) Narrate any additional method non-compliance or sample-specific anomaly.

Table VI B-1: Specific QC Requirements and Performance Standards for Hexavalent Chromium using WSC-CAM-VI B

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

[1] As per Appendix IV of MassDEP Policy #WSC-07-350, *MCP Representativeness Evaluations and Data Usability Assessments*, 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 Permanent and Temporary Solutions, including Permanent and Temporary Solutions on a portion of a disposal site, for preparation of Representativeness Evaluations and Data Usability Assessments pursuant to 310 CMR 40.1056(2)(k) and 40.1057(2)(k), respectively, 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 a Permanent or Temporary Solution submittal. The most current version of this document may be found at the following URL: http://www.mass.gov/dep/cleanup/laws/policies.htm#finpol.

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 B

3.1 General Reporting Requirements for WSC-CAM-VI B

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 B

Specific QC requirements and performance standards for WSC-CAM-VI B are presented in Table VI B-1. Specific reporting requirements for WSC-CAM-VI B are summarized below in Table VI B-2 as “Required Analytical Deliverables (**YES**)”. Requirements listed as “YES” must always be included as part of the laboratory deliverable for this method. It should be noted that data for those items listed as “NO” under “Required Analytical Deliverables” must be available for review during an audit and may also be requested for inclusion in the analytical deliverable 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 B-2 Routine Reporting Requirements for WSC-CAM-VI B (SW-846 7196A and 7199)

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***
Laboratory Control Sample (LCS)	***YES***
LCS Duplicate	***YES***
Matrix Spike Sample (MS) - Aqueous	***YES*** *(if requested by data user)*
Matrix Duplicate (MD) - Aqueous or Solid	***YES*** *(if requested by data user)*
Soluble Matrix Spike (MS) - Solid	***YES*** *(if requested by data user)*
Insoluble Matrix Spike (MS) - Solid	***YES*** *(if requested by data user)*
Post-digestion Spike (PDS) - Solid	***YES***
pH and ORP (Eh) - Solid (for each soil type and/or sediment matrix for each analytical batch)	***YES***
Duplicate Injections	***NO***
Identification and Quantitation	***NO***
General Reporting Issues	***YES***

3.2.2 Sample Dilution

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

The revised RL/LLOQ for the diluted sample, RL/LLOQ_d:

$$\text{RL/LLOQ}_d = \text{DF X Lowest Calibration Standard for Cr(VI)}$$

It should be understood that samples with elevated RLs/LLOQ as a result of a dilution may not be able to satisfy MCP standards/criteria in some cases if the RL/$LLOQ_d$ 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.

NOTE: **Over dilution is an unacceptable laboratory practice.** The post-dilution concentration of the target analyte must be detected within the calibration range.

Appendix VI B-1

Sample Collection, Preservation, and Handling Procedures for Hexavalent Chromium Analyses

Sample preservation, container and analytical holding time specifications for aqueous, soil, and sediment matrices for Hexavalent Chromium (Cr(VI)) conducted in support of MCP decision-making are summarized below and presented in Appendix VII-A of WSC-CAM-VII A, *Quality Assurance and Quality Control Guidelines for Sampling, Data Evaluation, and Reporting Activities for the Massachusetts Contingency Plan (MCP)*. Additional guidance may be found in SW-846, Chapter Three.

Matrix	**Container[1]**	**Preservation[5]**	**Holding Time[2]**
Concentrated Waste Cr(VI)	125 mL wide-mouth glass or polyethylene bottle	Cool to ≤ 6°C but not frozen.	30 days to digestion; 7 days from digestion to analysis. Store samples and alkaline digestates at 4 ± 2°C until analyzed.
Aqueous Cr(VI): SW-846 7196A	500 mL glass or polyethylene bottle	Cool to ≤ 6°C but not frozen.	24 hours
Dissolved/Filtered Cr(VI): SW-846 7196A	500 mL glass or polyethylene bottle	Filter (0.45 µm) on site or at the laboratory within 24 hours of collection, prior to analysis. Cool to ≤ 6°C but not frozen.	24 hours
Aqueous Cr(VI): SW-846 7199A	125 mL polyethylene bottle	Filter (0.45 µm) on site or at the laboratory within 24 hours of collection, prior to analysis. Adjust pH of sample to 9-9.5 with buffer solution (Section 5.7 of SW-846 Method 7199). If salts are formed after pH adjustment, the filtrate can be filtered again. Cool to ≤ 6°C but not frozen.	24 hours
Soil/Sediment Cr(VI)	4-ounce glass jar with teflon-lined cap[3]	Samples should be collected with non-metallic devices and stored field-moist at ≤ 6°C but not frozen.	30 days to digestion; 7 days from digestion to analysis[4]. Store samples and alkaline digestates at 4 ± 2°C until analyzed.
Soil/Sediment pH and ORP (Eh)	4-ounce glass jar with teflon-lined cap	Cool to ≤ 6°C but not frozen.	24 hours

[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*, if the holding time is exceeded by >2x, data users should consider nondetect results as unusable and positive results as estimated with a significantly low bias.**

[3] **If both Total Chromium and Cr(VI) are to be measured in a solid sample, separate sample jars must be collected for each analysis, such that the Cr(VI) sample container remains unopened until alkaline digestion commences.**

[4] **Soil/Sediment holding time as listed in SW-846 Method 3060A (December 1996).**

[5] **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 B-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 B (Hexavalent Chromium (Cr(VI): SW-846 7196A or SW-846 7199)**	
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; Refrigerator logs; Sample preparation logs (initial and final weights/volumes; preparation method reference); Filtration logs (if applicable)
Initial Calibration Data	Raw instrument data for initial calibration, including calculation of linear or non-linear regression and correlation coefficients; Concentrations of calibration standards used must be clearly presented.
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 for Cr(VI) for all samples and for pH and ORP (Eh) for solid samples	Sample result forms with dilution factors, units, RLs/LLOQs, method reference, date of preparation, date of analysis; raw instrument data, including duplicate injections for SW-846 7199; percent solids results
Method Blank Results	Method Blank results, units, RLs/LLOQs; raw instrument data
LCS/LCS Duplicate Results 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
MS Results – if analyzed: Soluble and Insoluble MS and PDS for solid samples **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
Soil/Sediment: pH of digestate during alkaline digestion (SW-846 Method 3060A)	pH documentation of digestate during alkaline digestion for all soil/sediment samples

Appendix VI B-3

Analysis Sequence for Hexavalent Chromium by WSC-CAM-VI B

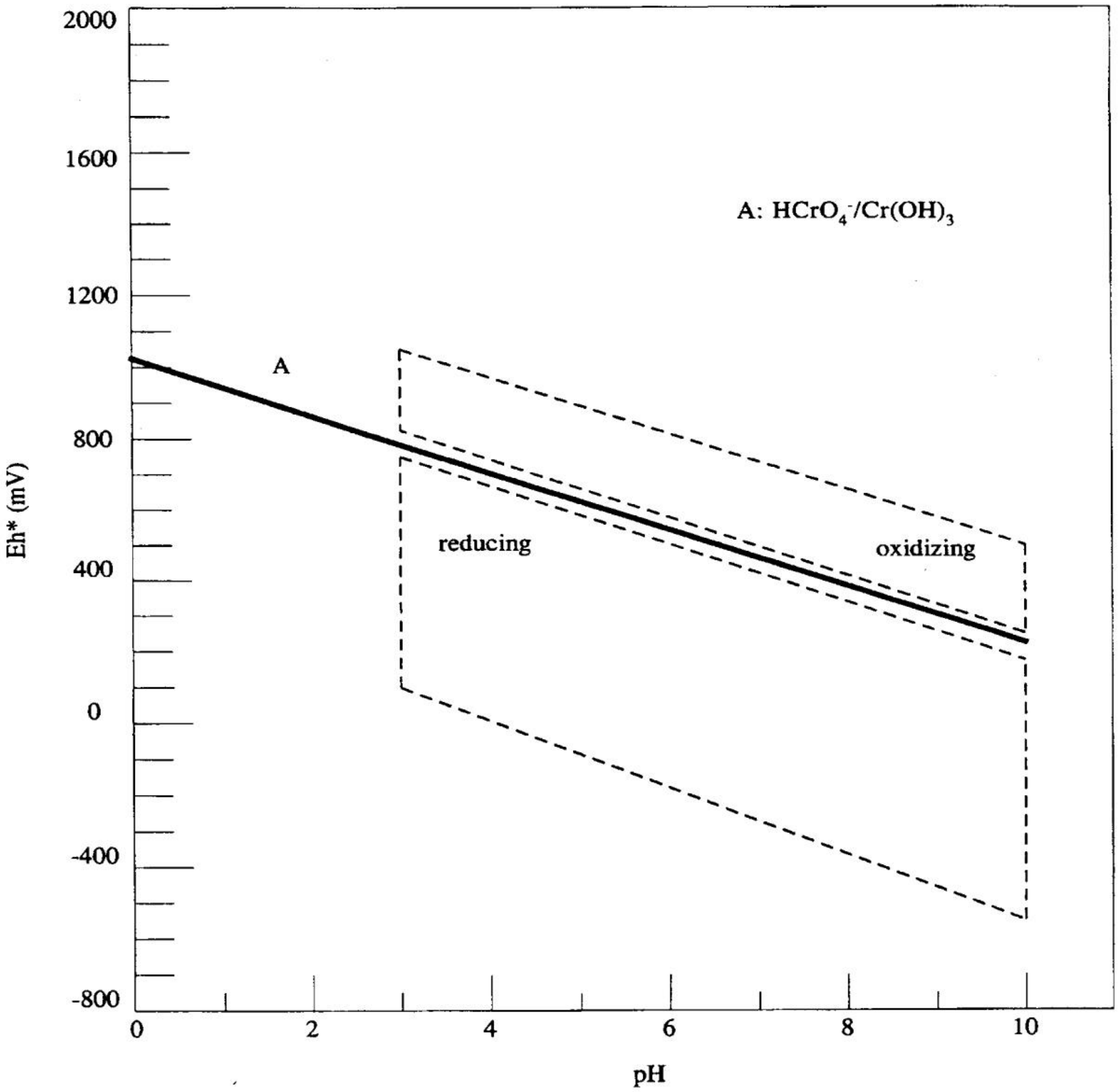
Typical analytical sequence for Hexavalent Chromium (Cr(VI)) using WSC-CAM-VI B:

- 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/LLOQ
- MB
- LCS
- LCSD – only required if not performing a project-specific MD
- 17 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 B-4

Eh/pH Phase Diagram

(**From:** SW-846 Method 3060A)



* Note the Eh values plotted on this diagram are corrected for the reference electrode voltage: 244 mV units must be added to the measured value when a separate calomel electrode is used, or 199 mV units must be added if a combination platinum electrode is used.