

State of Connecticut
Department of Energy and Environmental Protection
Recommended Reasonable Confidence Protocols
Quality Assurance and Quality Control Requirements
Hexavalent Chromium by Method 7196, SW-846

Version 3.0
May 2024

Written by the Connecticut DEEP QA/QC Workgroup

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Acronym List

<u>ACRONYM</u>	<u>DEFINITION</u>
CASN	Chemical Abstracts Service Number
CCB	Continuing calibration blank
CCV	Continuing calibration verification
Cr(III)	Trivalent Chromium
Cr(VI)	Hexavalent Chromium
%D	Percent difference
DEEP	CT Department of Energy and Environmental Protection
EP	Environmental Professional
g	Grams
GFAA	Graphite furnace atomic absorption
HCl	Hydrochloric acid
HCN	Hydrocyanic acid
HNO ₃	Nitric acid
ICB	Initial calibration blank
ICV	Initial calibration verification
ICP-AES	Inductively coupled plasma-atomic emission spectrometry
ICP-MS	Inductively coupled plasma-Mass Spectrometry
LCS/LCSD	Laboratory control sample / Laboratory control sample duplicate
LLCV	Low-level calibration verification
LLOQ	Lower limit of quantitation
MB	Method blank
MD	Matrix duplicate
mg/L	Milligram per liter
mg/kg	Milligram per kilogram
mL	Milliliter
MS	Matrix spike
nm	Nanometer
%R	Percent recovery
r/r ²	Correlation coefficient
RL	Reporting limit
RPD	Relative percent difference
RSR/RSRs	Remediation Standard Regulations
QA	Quality assurance
QC	Quality control
µg/L	Microgram per liter
µm	Micrometer

1.0 Quality Assurance and Quality Control Requirements for SW-846 Method 7196

1.1 Method Overview

SW-846 Method 7196 is used for the determination of hexavalent chromium ("Cr(VI)") by UV-Visible spectrophotometry. This analytical 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 3060, *Alkaline Digestion for Hexavalent Chromium*.

This document provides Quality Control ("QC") requirements and performance standards to be used in conjunction with the required analytical method SW-846 7196 for the analysis of aqueous and solid samples for Cr (VI). The QC requirements and performance standards specified in this document in Table 1A together with the analytical procedures described in EPA SW-846 Method 7196, *Chromium, Hexavalent (Colorimetric)* constitute the Reasonable Confidence Protocols.

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

1.2 Summary of SW-846 Method 7196

Dissolved Cr(VI), in the absence of interferences, may be determined colorimetrically by reaction with diphenylcarbazide in acid solution.

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-atomic emission spectrometry ("ICP-AES"), graphite furnace atomic absorption ("GFAA"), or ICP-mass spectrometry ("ICP-MS"). Refer to the appropriate Reasonable Confidence Protocol ("RCP") 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:

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

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.

1.2.1 Sample Digestion/Preparation Methods

Aqueous samples for analysis by SW846 Method 7196 do not require preparation/digestion prior to analysis, whereas solid samples (soil, sediment, sludge, waste) must be prepared/digested using SW-846 Method 3060, an alkaline digestion procedure for extracting Cr(VI) from solid samples. Alkaline digestion is the required preparative step for the analysis of soils, sediments, and sludges and similar waste material. The pH of the digestate must be carefully adjusted and monitored during the alkaline digestion to maintain the native chromium species in the environmental sample (i.e., prevent transformation of one species of chromium to another species). During sample digestion using SW-846 Method 3060, the pH must be maintained at pH 7.5 ± 0.5 to obtain a valid extract for analysis by SW-846 Method 7196.

To accurately measure all 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 3060 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 matrix spike ("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 1.3.2 of this RCP 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.

1.3 Method Interferences

1.3.1 Contamination Sources

Samples submitted to a laboratory for trace metal 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.

1.3.2 Chemical Interferences

The chromium reaction with diphenylcarbazide is usually free from interferences. However, certain substances may interfere if the chromium concentration is relatively low. Hexavalent molybdenum and mercury salts also react to form color with the reagent; however, the red-violet intensities produced are much lower than those for chromium at the specified pH. Concentrations of up to 200 mg/L of molybdenum and mercury can be tolerated. Vanadium interferes strongly, but concentrations up to 10 times that of chromium will not cause trouble.

Iron in concentrations greater than 1 mg/L may produce a yellow color, but the ferric iron color is not strong and difficulty is not normally encountered if the absorbance is measured photometrically at the appropriate wavelength.

Results for Cr(VI) for soils or wastes that contain levels of Cr(III) greater than 4x the reporting limit 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 magnesium in a phosphate buffer to the alkaline solution has been shown to suppress oxidation.

SW-846 Method 3060 is an alkaline digestion procedure for extracting hexavalent chromium (Cr (VI) from soluble, adsorbed, and precipitated forms of chromium compounds in soils, sludges, sediments, and similar waste materials. The pH of the digestate must be carefully adjusted and monitored during the digestion procedure. **Failure to meet the pH specifications of the method will necessitate re-digestion of the samples.**

The determination of the reducing/oxidizing tendency of each soil type and/or sediment matrix for each analytical batch is required for this method when measuring hexavalent chromium. This is accomplished by characterization of each sample for two (2) additional analytical parameters:

- pH (SW-846 Method 9045), and
- Oxidation Reduction Potential (ORP) (ASTM Method D 1498-93).

SW-846 Method 9045 should be referenced as the preparatory method for solid samples for ORP. The ORP and pH probes are inserted directly into the soil slurry. The displayed ORP and pH values are allowed to equilibrate and the resulting measurements are recorded. Additional optional parameters include:

- Ferrous iron (ASTM Method D3872-86), and
- Sulfides (SW-846 Method 9030).

Other indirect indicators of reducing/oxidizing tendency include:

- Total Organic Carbon (“TOC”),
- Chemical Oxygen Demand (“COD”), and
- Biological Oxygen Demand (“BOD”).

Analysis of these parameters establishes the tendency of Cr(VI) to exist or not exist in the un-spiked sample(s) and assists in the interpretation of QC data for matrix spike recoveries outside of the acceptance criteria.

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

1.3.3 Interfering Substances Present in Digestate

Certain substances, not typically found in the alkaline digestates of soils, may interfere in the analytical methods for Cr(VI) following alkaline extraction if the concentrations of these interfering substances are high and the Cr(VI) concentration is low. Reducing agents such as soluble fulvic acids, which are sometimes present in alkaline digestates, may also be potential interferents for this method. Analytical techniques that reduce bias caused by co-extracted matrix components may be effective to minimize these biases after validation of their performance.

1.4 Quality Control Requirements for SW-846 Methods 7196

1.4.1 Reporting Limits/ Lower Limits of Quantitation for SW-846 Method 7196

The reporting limit (“RL”), or lower limit of quantitation (“LLOQ”), for an individual analyte is dependent on the concentration of the lowest non-zero standard in the initial calibration or the low-level calibration verification (“LLCV”), sample weight/volume, preparation factors, percent solids, dilution factors, etc., as required. Table 1.0 lists approximate RL/LLOQs for various matrices utilizing spectrophotometry. Solid matrices in this table assume 100% solids.

Table 1.0: Typical Reporting Limits / Lower Limits of Quantitation¹

Matrix	Typical Reporting Limit
Aqueous	5 to 10 µg/L
Soil and Sediment (assuming 100% solids)	0.5 to 1.0 mg/kg

¹Note these values are intended to serve as guidance to EPs when planning analytical needs to achieve the data quality objectives to meet project-specific goals. These tables are not intended to dictate what RL/LLOQs laboratories must report.

Moisture content of soils and sediments will raise the RL/LLOQ, as all results must be reported on a dry weight basis for these two matrices. Sample dilution or lower sample weight/volume will also cause the RL/LLOQ's to be raised. It is the responsibility of the data user, in concert with the laboratory, to establish the range and required RL/LLOQ for the target analytes to meet the project Data Quality Objectives (“DQOs”). To meet the RLs/LLOQs

applicable to project DQOs, it may be necessary to modify the analytical method to improve sensitivity. In such cases, the modifications must be noted in the laboratory report narrative.

1.4.2 General Quality Control Requirements

This protocol is restricted to use by, or under the supervision of, analysts who are experienced in using spectrophotometry as a quantitative tool and skilled in the correction of chemical and physical interferences described in this method.

Refer to SW-846 Chapter One for general QC procedures for all analytical methods, including SW-846 Method 7196. These requirements ensure that each laboratory maintain a formal quality assurance (“QA”) program and records to document the quality of all inorganic data and be certified by the Connecticut Department of Public Health for the analysis performed. QC procedures necessary to evaluate the instrument’s operation may be found in SW-846 Chapter 3 and SW-846 7196 and include evaluation of calibrations and performance of sample analyses. Instrument QC and method performance requirements for other instrumentation, such as ICP-AES, ICP-MS, or GFAA can be found in their respective SW-846 methods.

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

Laboratories must document and have on file an IDOC for each combination of sample preparation and determinative method being used. An IDOC must be completed and documented when a method is initially started up, whenever a method is substantially modified, or new laboratory staff is trained to perform this Method. These limits must meet or fall within the limits specified in Section 1.4 and Table 1A of this RCP. See SW-846 Chapter One and SW-846 Methods 3060 and 7196 for the procedure. The IDOC must include the following elements provided in Table 2.0:

Table 2.0: IDOC Requirements

QC Element	Performance Criteria
Initial Calibration	Table 1A
Continuing Calibration	Table 1A
Method Blanks	Table 1A
Percent Recovery for MS/LCS	Table 1A
Relative Percent Difference of Matrix Duplicate	Table 1A
Soluble and insoluble hexavalent chromium matrix spike for solid samples only.	Table 1A

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

1.4.3 Specific QA/QC Requirements and Performance Standards for SW-846 Method 7196

Specific QA/QC requirements and performance standards for SW-846 Method 7196 are presented in Table 1A. Strict compliance with the QA/QC requirements and performance standards for this method, as well as satisfying

other analytical and reporting requirements will provide the EP with “Reasonable Confidence” regarding the usability of analytical data to support environmental decisions. The concept of “Reasonable Confidence” is explained on the CT Department of Energy and Environmental Protection (“DEEP”) website.

While optional, parties electing to utilize these protocols will be assured that agency reviewers will, generally, accept “Reasonable Confidence” data. To achieve “Reasonable Confidence” parties must:

1. Comply with the applicable QC analytical requirements prescribed in Table 1A for this test procedure;
2. Evaluate and narrate all protocol non-compliances and implement, as necessary, required corrective actions and analytical response actions for all non-conforming analytical performance standards; and
3. Retain reported and unreported analytical data and information for a period of 5 years or as required under applicable accreditation criteria.

Table 1A: Specific QA/QC Requirements and Performance Standards for SW-846 Method 7196

Required QC Parameter	Data Quality Objective	Required Performance Standard	Required Deliverable	Required Corrective Action	Analytical Response Action
Initial Demonstration of Capability ("IDOC")	Laboratory Analytical Accuracy & Precision	(1) Must be performed prior to using method samples. (2) Must be performed for each matrix. (3) Must follow requirements in Section 1.4 of this protocol.	No	Refer to Section 1.4.2 of this protocol.	NA
Preparation of Samples	Accuracy & Representativeness	(1) For Hexavalent Chromium, Cr (VI), solid samples must be pretreated/digested prior to analysis. See SW-846-7196, 3060, and Section 1.2.1 of this RCP protocol for appropriate preparation procedures. NOTE: pH of alkaline digestates of solid samples must be maintained at 7.5 ± 0.5 . Follow requirements in SW-846 3060. No special preparation for aqueous samples. (2) Additional measurements of pH and ORP (Eh) are required for soil/sediment samples. See Section of this RCP protocol for further details.	No	NA	NA
Initial Calibration ("ICAL")	Laboratory Analytical Accuracy	(1) Frequency: Daily prior to sample analysis. (2) Minimum of calibration blank plus five calibration standards. (3) Low-level standard in calibration must be at or below the RL/LLOQ. (4) Linear regression with correlation coefficient $r \geq 0.995$.	No	Perform instrument maintenance as necessary; recalibrate as required by method.	Analysis is suspended until initial calibration meets criteria.

Required QC Parameter	Data Quality Objective	Required Performance Standard	Required Deliverable	Required Corrective Action	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: undigested. (3) Concentration level near mid-point of curve. (4) Percent recovery must be 85-115%.	No	Reanalyze ICV; if acceptable; no further action required. If reanalysis is still outside the criteria, recalibrate and reanalyze ICV.	Suspend analyses until ICV meets criteria.
Initial Calibration Blank ("ICB")	Laboratory analytical Sensitivity (Instrument drift & contamination)	(1) Frequency: immediately after ICV (2) Undigested. (3) Cr (VI) must be <RL/LLOQ.	No	(1) Reanalyze ICB; if acceptable, no further action required. (2) If reanalysis is still outside of criteria, recalibrate and reanalyze ICV and 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) Frequency: daily prior to sample analysis. If calibration includes the RL/LLOQ as the low-level standard in 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	(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 laboratory report 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.

Required QC Parameter	Data Quality Objective	Required Performance Standard	Required Deliverable	Required Corrective Action	Analytical Response Action
Continuing Calibration Verification ("CCV")	Laboratory Analytical Accuracy	(1) Frequency- every 10 samples and at the end of the analytical run (2) Prepared using same source as initial calibration standards: undigested (3) Concentration level near midpoint of curve (4) Percent recovery must be 85-115%.	No	(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 (>115%) and all associated sample results are non-detected, no corrective action required.	If (3) applies, include explanation in laboratory report narrative.

Required QC Parameter	Data Quality Objective	Required Performance Standard	Required Deliverable	Required Corrective Action	Analytical Response Action
Continuing Calibration Blank ("CCB")	Laboratory Analytical Sensitivity (instrument drift & contamination)	(1) Frequency – every 10 field samples following CCV and at the end of the analytical run (2) Un-digested. (3) Cr (VI) must be <RL/LLOQ.	No	(1) Reanalyze CCB; if acceptable, no further action required. (2) If analysis 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 CBB 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.	If (3) applies, include explanation in laboratory report narrative.

Required QC Parameter	Data Quality Objective	Required Performance Standard	Required Deliverable	Required Corrective Action	Analytical Response Action
Method Blank ("MB")	Laboratory Method Sensitivity (contamination evaluation)	(1) Frequency- one per analytical or digestion batch, or every 20 field samples (2) Must be prepared/digested with samples using the same preparation method as the samples. (3) Cr (VI) must be <RL/LLOQ (4) Matrix specific and matrix matched.	Yes	(1) Reanalyze MB; if acceptable, no further action required. (2) If analysis is still outside of criteria, re-digest and reanalyze MB and all associated samples in batch- unless (3) applies. (3) If concentration of Cr (VI) in MB is > RL/LLOQ but all associated sample results are either non-detected or >10x concentration of Cr (VI) in MB level, no corrective action required.	If (3) applies, include explanation in laboratory report narrative.
Laboratory Control Sample ("LCS")	Laboratory Method Accuracy	(1) Frequency – One per analytical or digestion batch or every field ≤20 samples (2) Must be matrix-matched by digesting with the samples using the same preparation method. It is recommended that 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 aqueous LCS near mid-point of curve. (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) Matrix specific (solid, aqueous, etc.).	Yes	(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 associated field samples in batch.	Report non-conformances in laboratory report narrative.

Required QC Parameter	Data Quality Objective	Required Performance Standard	Required Deliverable	Required Corrective Action	Analytical Response Action
LCS Duplicate ("LCSD")	Laboratory Analytical Accuracy & Precision	<p>(1) Frequency: One per analytical or digestion batch of ≤20 field samples ONLY if not performing project-specific MD.</p> <p>(2) Must be matrix-matched by digesting with the samples using the same preparation method. It is recommended that a solid SRM be prepared and analyzed with solid field samples as the "solid LCSD." An SRM is a soil or sediment matrix that contains hexavalent chromium at a known concentration and with 95% confidence limits.</p> <p>(3) Concentration level must be same as LCS. Analyze immediately following LCS.</p> <p>(4) Percent recovery for Cr (VI) must be 80-120% for aqueous LCS and within vendor control limits (95% confidence limits) for solid LCS.</p> <p>(5) RPDs must be ≤20% for aqueous LCS/LCSD and ≤30% for solid LCS/LCSD.</p>	Yes	<p>(1) Reanalyze LCSD; if acceptable, no further action required.</p> <p>(2) If reanalysis is still outside of recovery criteria for Cr(VI) and LCS is in-control for Cr (IV), no corrective action required.</p> <p>(3) If LCSD and LCS are both outside of recovery criteria, re-digest and all associated field samples in batch.</p>	Report recovery and RPD exceedances in laboratory report narrative.
Matrix Spike ("MS") Site Specific Aqueous Samples Only	Method Accuracy in Sample Matrix	<p>(1) Frequency: one per digestion batch of ≤20 field samples per matrix is strongly recommended (designated by data user on COC or at project set-up).</p> <p>(2) Percent recovery must be 75-125%.</p>	Yes (if requested by data user)	<p>(1) Reanalyze MS; if acceptable, no further action required.</p> <p>(2) After reanalysis, if MS recovery is 30-74% or >125% and LCS was in control, no corrective action is required.</p> <p>(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.</p>	<p>Report MS non-conformance in laboratory report narrative.</p> <p>If re-digested due to recoveries <30%, report both sets of sample/MS data.</p>

Required QC Parameter	Data Quality Objective	Required Performance Standard	Required Deliverable	Required Corrective Action	Analytical Response Action
<u>Soluble Cr⁶⁺ Matrix Spike ("MS") Site Specific Solid Samples Only</u>	Method Accuracy in Sample Matrix	(1) Frequency: one per ≤20 field samples per matrix designated by data user on COC or at project set-up. (2) Soluble spike = Potassium Chromate (K ₂ Cr ₂ O ₇) (3) Percent recovery of Cr (VI) must be 75-125%.	Yes (if requested by data user)	(1) Evaluate LCS. If LCS within acceptance limits, evaluate pH/Eh of sample using figure in Appendix A of this RCP. Alternatively, perform mass balance as per SW-846 3060. If reducing conditions exist, no further action required. If reducing conditions do not exist: (2) Reanalyze MS; if acceptable, no further action required. (3) After reanalysis, if MS recovery is 30-74% or >125% and LCS was in control, no corrective action is required. (4) If MS recovery is <30% and associated with non-detected results, re-digest (homogenize sample well) and reanalyze samples/MS pair. Report results and narrate.	Report MS non-conformances in laboratory report narrative and note oxidation/reduction characteristics of samples. If re-digested due to recoveries <30%, report both sets of sample/MS data.

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<u>Insoluble Matrix Spike ("MS") Site Specific Solid Samples Only</u>	Method Accuracy in Sample Matrix	(1) Frequency- 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 (if requested by data user)	Evaluate LCS. If LCS within acceptance limits, evaluate pH/Eh of sample using figure in Appendix A of this RCP. Alternatively, perform mass balance as per SW-846 3060. If reducing conditions exist, no further action required. If reducing conditions do not exist: (i) Reanalyze MS; if acceptable, no further action required. (ii) After reanalysis, if MS recovery is 30-74% or >125% and LCS was in control, no corrective action is required. (iii) 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. Reanalyze, lab narrates outliers; possible usability issue.	Report MS non-conformances in laboratory report narrative and not oxidation/reduction characteristics of sample. If re-digested due to recoveries <30%, report both sets of sample/MS data.
Matrix Duplicate ("MD")	Method Precision in Sample Matrix	(1) Frequency: one per digestion batch of ≤20 field samples per matrix is strongly recommended	Yes (if requested by data user)	Narrate.	Note non-conformances in

Required QC Parameter	Data Quality Objective	Required Performance Standard	Required Deliverable	Required Corrective Action	Analytical Response Action
Site Specific		(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.			laboratory report narrative.

Required QC Parameter	Data Quality Objective	Required Performance Standard	Required Deliverable	Required Corrective Action	Analytical Response Action
General Reporting Issues	NA	<p>(1) Measurements of ORP (as Eh) and pH must be performed and reported for each solid matrix type.</p> <p>(2) Non-detected values must be reported with the sample-specific RL/LLOQ for Cr (VI) using all appropriate preparation/dilution factors.</p> <p>(3) The lab must only report values \geq the sample-specific RL/LLOQ.</p> <p>(4) Sample concentrations that exceed the highest calibration standard must be diluted and reanalyzed to fall within the linear calibration range.</p> <p>(5) Results for soils/sediments must be reported on a dry-weight basis for comparison to RSR regulatory standards.</p> <p>(6) Results must be reported with 2 or more "significant figures" if \geq RL/LLOQ</p> <p>(7) Concentrations below the RL/LLOQ should be reported as "ND" with the sample specific RL/LLOQ also reported.</p>	NA	NA	<p>(1) The performance of dilutions must be documented in the laboratory report narrative or on the report form. Unless due to elevated concentrations of Cr (VI), reasons for dilutions must be explained in laboratory report narrative.</p> <p>(2) If samples are not preserved properly or are not received with an acceptable cooler temperature, note the non-conformances in the laboratory report narrative.</p> <p>(3) If samples are digested and/or analyzed outside of the holding time, note the non-conformances in the laboratory report narrative.</p> <p>(4) Narrate any additional method non-compliance or sample-specific anomaly.</p>

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1.5 Routine Reporting Deliverables for Method 7196

The following table (Table 3.0) lists the routine report deliverables. Note that while laboratories are not required to report certain items, they must keep the data on file and may be required to report all items in special circumstances.

Table 3.0: Report Deliverables

Parameter	Deliverable	Comments
Sample Preparation Data	NO	Data on file at laboratory
Initial Calibration	NO	Correlation coefficient must meet QA/QC requirements
Initial Calibration Verification Standard	NO	ICV must pass
Initial Calibration Blank	NO	Note non-conformances in laboratory report narrative
Continuing Calibration Verification	NO	CCV must pass
Continuing Calibration Blank	NO	Note non-conformances in laboratory report narrative
Method Blanks	YES	Note non-conformances in laboratory report narrative. Flag all positive sample results above RL/LLOQ with "B" flag.
Lab Control Sample/LCS Duplicate	YES	Note non-conformances in laboratory report narrative
Site-Specific Matrix Spike/ Matrix Duplicate (Both soluble and insoluble spikes if analyzed)	YES (If analyzed)	Note non-conformances in laboratory report narrative
General Reporting Issues	YES	Note non-conformances in laboratory report narrative
QA/QC Certification Form	YES	Signed by laboratory director or their designee.
pH and ORP (Eh) – Solid (for each soil type and/or sediment matrix for each analytical batch)	YES	
Chain-of-Custody Form	YES	Signed by sample collector, courier, and laboratory

1.5.1 Reporting and Flagging of Results

The following rules apply to reporting results:

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

1.8 Sample Containers, Preservations, and Holding Times

Table 4.0 identifies the type of containers, preservation requirements, and holding times dependent upon analyte and matrix.

Table 4.0: Sample Containers, Preservation and Holding Times

Matrix	Container ^{1,2,3}	Preservative ⁴	Holding Time
Aqueous (total)	500 mL plastic† or glass	Cool to 4 ± 2° C If dissolved Cr ⁶⁺ to be determined filter thru 0.45 µm filter prior to analysis	24 hours
Aqueous (dissolved)	500 mL plastic† or glass	Filter thru 0.45 µm filter prior to analysis, then cool to 4 ± 2° C	24 hours
Soil/Sediment samples.	250 mL glass jar or plastic bottle with Teflon or plastic lined cap.	Cool to 4 ± 2° C	Digest within 30 days. Analyze digestate within 7 days of preparation.
High Concentration Waste Samples	250 mL glass jar or plastic bottle with Teflon or plastic lined cap.	Cool 4 ± 2° C.	Digest within 30 days. Analyze digestate within 24-hrs of preparation.
Soil/sediment pH and ORP	250 mL glass jar or plastic bottle with Teflon or plastic lined cap.	Cool to 4 ± 2° C	24 hours
Soil / sediment Ferrous iron and sulfide	250 mL glass jar or plastic bottle with Teflon or plastic lined cap.	Cool to 4 ± 2° C	7 days

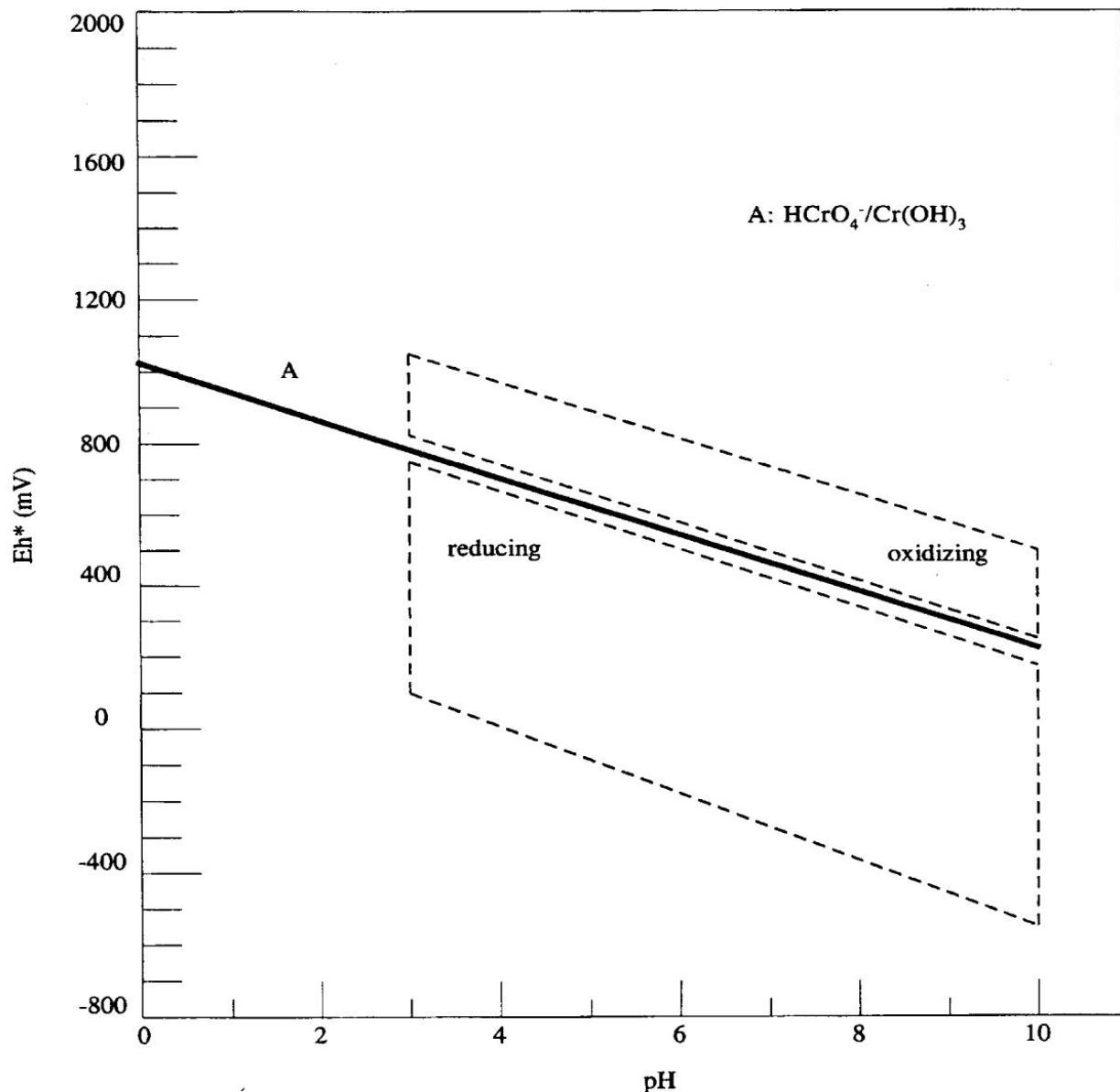
¹The collection of multiple sample containers per sample location may be required to collect enough sample for matrix QC.

²If 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.

³Separate containers are required for each method: hexavalent chromium, pH and ORP, and ferrous iron and sulfide.

⁴If 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 6°C are acceptable.

Appendix A: Eh/pH Phase Diagram



* 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.