

State Of Connecticut  
Department of Environmental Protection

Recommended Reasonable Confidence Protocols

Quality Assurance and Quality Control Requirements

Determination of Hexavalent Chromium By SW-846 Method 7196

Version 2.0  
July 2006

Written by the Connecticut DEP QA/QC Workgroup

Revision	Comments	Date
1.0	First version for publication	7/05
2.0	Final version based upon public comments	July 2006

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**1.0 QA/QC Requirements for Method 7196**

**1.1 Method Overview**

Method 7196 is used to determine the concentration of dissolved hexavalent chromium [Cr(VI)] in EP/TCLP characteristic extracts and ground waters. This method may also be applicable to certain domestic and industrial wastes, provided that no interfering substances are present.

Soil, sediment and other solid type samples require alkaline digestion using SW-846 Method 3060A. The digestate can then be analyzed by this method for hexavalent chromium

Method 7196 may be used to analyze samples containing from 0.5 to 50 mg of Cr(VI) per liter.

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

## 1.2 Summary Of Method

Dissolved hexavalent chromium, in the absence of interfering amounts of substances such as molybdenum, vanadium, and mercury, may be determined colorimetrically by reaction with diphenylcarbazide in acid solution. A red-violet color of unknown composition is produced. The reaction is very sensitive, the absorbancy index per gram atom of chromium being about 40,000 at 540 nm. Addition of an excess of diphenylcarbazide yields the red-violet product, and its absorbance is measured photometrically at 540 nm.

1.2.1 Soil and solid samples must be digested prior to analysis to solubilize the hexavalent chromium without oxidizing the existing trivalent chromium or reducing any hexavalent chromium present. SW-846 Method 3060A has been found adequate for this purpose for most soil/solid matrices.

1.2.2 Under the alkaline conditions of the Method 3060A extraction, minimal reduction of Cr (VI) or oxidation of native Cr (III) occurs. The addition of  $Mg^{+2}$  in a phosphate buffer to the alkaline solution has been shown to suppress oxidation. The efficiency (as % Recovery) of the extraction procedure is assessed using spike recovery data for soluble and insoluble forms of Cr (VI) (e.g.,  $K_2Cr_2O_7$  and  $PbCrO_4$ ), coupled with the measurement of other soil properties, such as oxidation reduction potential (ORP), pH, organic matter content, ferrous iron, and sulfides as indicators that oxidative conditions will be maintained during digestion of the Cr (VI) spike.

Recovery of an insoluble Cr (VI) spike is used to assess efficiency and maintenance of non-reductive conditions during the solubilization 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)<sub>3</sub>.

1.2.3 Trivalent chromium is defined as the difference between the total chromium concentration and the hexavalent chromium concentration ( $Cr^{3+} = \text{Total Cr} - Cr^{6+}$ ). Total chromium may be determined by methods 6010, 6020, or by graphite furnace atomic absorption spectroscopy.

### **1.3 Reporting Limits for Method 7196**

The reporting limit (RL) for the colorimetric method is based upon the lowest standard in the calibration curve, sample weight/volume, any dilutions, and for soils/sediments the percent moisture.

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

It is the responsibility of the EP to specify to the laboratory the detection limits required for the samples. In order to meet the limits it may be necessary to modify the analytical method by using increased sample volume or mass, concentration of the digestate, etc. In such cases the modifications must be noted in the narrative.

### **1.4 Interferences**

1.4.1 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.

1.4.2 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.

1.4.3 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.**

1.4.4 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 9045C), and
- Oxidation Reduction Potential (ORP) (ASTM Method D 1498-93).

Section 7.2 of SW-846 Method 9045C 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 9030B).

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 unspiked sample(s) and assists in the interpretation of QC data for matrix spike recoveries outside of the acceptance criteria.

#### 1.4.5 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. Refer to Section 1.4.1 for a discussion of the specific metals that may interfere with Cr (VI) quantification. 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.1.5 General Quality Control Requirements

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

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

**Table 1.0 IDOC Requirements**

<b>QC Element</b>	<b>Performance Criteria</b>
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

**1.5 Quality Control Requirements for SW-846 Methods 3060A and 7196**

1.5.1 General Quality Control Requirements for Determinative Inorganic Methods

Refer to SW-846 Chapter One for general quality control procedures for all inorganic methods, including SW-846 Methods 3060A and 7196. These requirements ensure that each laboratory maintain a formal quality assurance program and records to document the quality of all inorganic data.

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

### 1.5.2 Specific QA/QC Requirements and Performance Standards for SW-846 Methods 3060A and 7196

Specific QA/QC requirements and performance standards for SW-846 Methods 3060A and 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 environmental professional (EP) with “Reasonable Confidence” regarding the usability of analytical data to support DEP decisions.

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

1. Comply with the applicable QC analytical requirements prescribed in Table 1A for this test procedure;
2. Evaluate and narrate, as necessary, compliance with performance standards prescribed in Table 1A for this test method; and
3. Adopt the reporting formats and elements specified in Section 1.7 of this method.

### 1.5.3 Site Specific Matrix Spike (MS) and Matrix Duplicate (MD) Samples

It is strongly recommended that site specific MS/MD samples be analyzed from each site, and each matrix type sampled. Percent recovery data from site specific samples allow the EP to make informed decisions regarding contamination levels at the site. Batch MS/MD results do not give any indication of site specific matrix interferences or analytical problems related to the specific site matrices and are in general discouraged. Field blanks, rinsate blanks, etc. should not be used for MS/MD's. A laboratory may substitute a matrix spike/matrix spike duplicate in lieu of the MS/MD.

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**Table 1A Specific QA/QC Requirements and Performance Standards for Methods 3060A and 7196\***

Required QA/QC Parameter	Data Quality Objective	Required Performance Standard	Required Deliverable	Recommended Corrective Action	Analytical Response Action
Preparation of Samples	Accuracy and Representativeness	All soil solid samples must be digested by Method 3060A prior to analysis. See Methods 3060A for details. No special preparation for aqueous samples.	NO		
Initial Calibration	Laboratory Analytical Accuracy	1) At least every six months or whenever ICV fails. 2) Minimum of calibration blank plus five calibration standards. Low standard must be $\leq$ RL. 3) Linear curve with "r" $\geq$ 0.995.	NO	Recalibrate as necessary.	Sample analysis cannot proceed without valid initial calibration.
Initial Calibration Verification (ICV)	Laboratory Analytical Accuracy	1) Daily and prior to sample analysis 2) 2 <sup>nd</sup> source std in mid-range or vendor supplied value. 3) ICV $\pm$ 20% of true value. 4) ICV concentration must be within calibration curve range.	NO	Re-calibrate/Re-analyze ICV as required by method.	Suspend all analyses until problem corrected and ICV meets criteria.
Continuing Calibration Verification (CCV)	Laboratory Analytical Accuracy	1) Every 10 samples and at end of analytical sequence. 2) Can be same source or second source. 3) Recovery $\pm$ 20% of true value	NO	Recalibrate/Re-analyze all samples since last compliant CCV	Report non-conformances in narrative..



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**Table 1A Specific QA/QC Requirements and Performance Standards for Methods 3060A and 7196\* (continued)**

Required QA/QC Parameter	Data Quality Objective	Required Performance Standard	Required Deliverable	Recommended Corrective Action	Analytical Response Action
Continuing Calibration Blank (CCB)	Evaluation of instrument drift, sensitivity, and contamination.	1) Every 10 samples immediately after CCV. 2) CCB must be < RL	NO	Recalibrate/Re-analyze all samples since last compliant CCB	Report non-conformances in narrative.
Method Blanks	Laboratory Contamination Evaluation	1) Digested every 20 or every batch, whichever is greater. 2) Matrix specific and matrix matched 3) Cr6+ must be <RL	YES	Locate source of contamination and correct problem. Reprepare samples unless all detected analyte concentrations >10x method blank level	Report non-conformances in case narrative.
Laboratory Control Sample (LCS)	Laboratory Method Accuracy	1) Every 20 samples or each batch, whichever is more frequent 2) Standard source different from initial calibration source. 3) Matrix specific (solid, aqueous, etc). 4) LCS recoveries $\pm 20\%$ for aqueous media and within vendor control (95% confidence limits) for solids.	YES	Redigest and reanalyze all samples.	Report non-conformances in narrative.

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**Table 1A Specific QA/QC Requirements and Performance Standards for Methods 3060A and 7196\* (continued)**

Required QA/QC Parameter	Data Quality Objective	Required Performance Standard	Required Deliverable	Recommended Corrective Action	Analytical Response Action
Site Specific Matrix Spike  <i>Aqueous Samples Only</i>	Accuracy in Sample Matrix	1) Every 20 samples or batch per matrix** 2) Percent recovery limits must be between 75-125%.	Yes**(If analyzed)	If LCS in criteria, note in narrative. If LCS out of criteria, reprepare/reanalyze samples & LCS.	Note outliers in narrative
Site Specific Matrix Duplicate	Precision in Sample Matrix	1) Every 20 samples or batch per matrix** 2) For aqueous samples if sample results > 5x the RL, RPD ≤ 20%, soils ≤35%. If sample results <5x the RL, aqueous RPD limit is ± the RL, soil limit ≤ 2x the RL.	Yes** (If analyzed)	None	Note outliers in narrative.
Site Specific Soluble Cr6+ Matrix Spike  <i>Solid Samples Only</i>	Accuracy in Sample Matrix	1) Every 20 samples or batch** 2) Percent recovery limits must be between 75-125%.	Yes**(If analyzed)	If LCS in criteria evaluate oxidation/reduction characteristics of sample. Alternatively perform mass balance per Method 3060A.If reducing conditions exist note in narrative.	Note outliers in narrative. Note oxidation/reduction characteristics.

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**Table 1A Specific QA/QC Requirements and Performance Standards for Methods 3060A and 7196\* (continued)**

Required QA/QC Parameter	Data Quality Objective	Required Performance Standard	Required Deliverable	Recommended Corrective Action	Analytical Response Action
Site Specific Soluble Cr6+ Matrix Spike  <i>Solid Samples Only</i>	Accuracy in Sample Matrix	1) Every 20 samples or batch** 2) Percent recovery limits must be between 75-125%.	Yes**(If analyzed)	If LCS in criteria evaluate oxidation/reduction characteristics of sample. Alternatively perform mass balance per Method 3060A.If reducing conditions exist note in narrative.	Note outliers in narrative. Note oxidation/reduction characteristics.
General Reporting Issues	N/A	1) The laboratory should report only concentrations detected above the sample specific RL. 2) Concentrations below the reporting limit (RL) should be reported as “ND” with the sample specific RL also reported 3) Dilutions: If analyte above linear range, dilute and reanalyze for those analytes. 4) Soils/sediments reported on a dry weight basis. 5) A low level calibration standard must be at or below the RL.	YES	N/A	

Notes for Table 1A:

\* Refers to latest published version of SW-846 Methods 3060A and 7196.

RPD = Relative Percent Difference

%RSD = Relative Percent Standard Deviation

EP=Environmental Professional

r = Correlation Coefficient

N/A = Not Applicable

### 1.6 Routine Reporting Deliverables for Methods 3060A and 7196

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

The following rules apply to reporting results:

Non-Detects: Report all non-detects and results below the reporting limit as “ND” (Not Detected at the specified Reporting Limit). The reporting limit for each compound in each sample must be listed on the report and take into account the exact sample mass, any dilution factors, percent moisture, etc.

Compounds detected above the reporting limit in blanks and found in samples, also above the reporting limit, shall be flagged with a “B” suffix (e.g. 25B). All soil/sediment results shall be reported on a dry weight basis.

**Table 1.1 Report Deliverables**

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

**Table 2A Sample Containers, Preservation and Holding Times**

<b>MATRIX</b>	<b>CONTAINER</b>	<b>PRESERVATIVE</b>	<b>HOLDING TIME</b>
Aqueous	500 mL plastic† or glass	Cool to $4 \pm 2^\circ \text{C}$ If dissolved $\text{Cr}^{6+}$ to be determined filter thru $0.45 \mu\text{m}$ filter prior to analysis	24 hours
Soil/Sediment samples.	250 mL glass jar or plastic bottle with Teflon or plastic lined cap.	Cool to $4 \pm 2^\circ \text{C}$	Digest within 30days. 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 $4 \pm 2^\circ \text{C}$ .	Digest within 30days. 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 $4 \pm 2^\circ \text{C}$	24 hours
Soil / sediment Ferrous iron and sulfide	250 mL glass jar or plastic bottle with Teflon or plastic lined cap.	Cool to $4 \pm 2^\circ \text{C}$	7 days

Notes:

† Plastic bottles must be acid rinsed and either high-density polyethylene or Teflon.  
 The number of sample containers is optional. Laboratories should supply enough containers to allow for any reanalysis or breakage.