

Method 0061 for Hexavalent Chromium (Cr⁺⁶)

Fundamentals of the Method for Analysis of Hexavalent Chromium in Method 0061 Train Samples

Collection and Analysis of Method 0061 Train Samples

Stack gas samples for hexavalent chromium (CAS No. 7440-47-3) should be collected using a standard hexavalent chromium recirculatory train, as described in SW-846 Method 0061. The first impinger solution, aqueous 1.0N potassium hydroxide, is recirculated continuously through the train's probe to capture and stabilize stack gas hexavalent chromium. The method requires that the hexavalent chromium train use all Teflon™ (or Teflon™-lined) impingers and connecting glassware. After completing each run, the impingers of the train will be connected to a purified nitrogen gas source and purged slowly, as specified in Method 0061. The impinger catches will be filtered under pressure on site and then collected for transport to the analytical laboratory. The purpose of the nitrogen gas purging and filtration steps is to preserve and stabilize the hexavalent chromium, if present, in the ⁺⁶ oxidation state.

To assess the stability of the sampled hexavalent chromium, the impinger sample composites for each hexavalent chromium train collected will be divided into aliquots and spiked as described below. The train aliquots will be analyzed by the laboratory to determine the native concentrations, and spike recoveries in the actual stack gas matrix. This procedure is being implemented in lieu of a 24-hour holding time requirement for hexavalent chromium samples.

Hexavalent Chromium Train Stability Samples (Field Spikes)

The sampling coordinator will prepare hexavalent chromium stability samples. Hexavalent chromium stability samples consists of field spikes that are analyzed to demonstrate that the native hexavalent chromium, when collected in the 1.0N potassium hydroxide impinger solution stack gas matrix and preserved according to the method, is stable over the time period between sample collection and subsequent sample analysis. Aliquots of the actual hexavalent chromium impinger samples will be spiked at the time of sample recovery at 10 parts per billion (ppb) and 25 ppb with a hexavalent chromium spiking standard of 1 µg per liter (L), which will be prepared in the field by the sampling team.

In addition to these spikes, one aliquot of the impinger samples will be analyzed without any spike added to determine the native concentration of hexavalent chromium in each train sample during each run. One aliquot of the potassium hydroxide impinger reagent solution also will be collected and spiked in this way to assess the overall spike recovery and method accuracy as a blank spike sample. Field and blank spikes will be applied in the field after sample recovery, but prior to shipment of samples from the associated run. All spiked aliquots will be analyzed by the laboratory and the spike recoveries will be calculated. Good recovery of hexavalent chromium in the train spike samples (greater than 70 percent) should indicate that the hexavalent chromium trapped in the 1.0N potassium hydroxide matrix remains in that oxidation state through analysis, and verifies that the sample concentrations are representative of the "true" hexavalent chromium concentration in the stack gas. All samples submitted for analysis for hexavalent chromium will be analyzed within 14 days of collection. All data from the stability demonstration will be reported and discussed in detail in the CPT report.

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Hexavalent Chromium Emissions in Stack Gas

SAMPLE PRESERVATION AND HOLDING TIMES

All samples requiring refrigeration will be placed on ice (when required for preservation) in coolers during and after sampling and will be stored at a temperature of approximately 4°C until analyzed. In addition to cooling all samples that require low temperature preservation, chemical preservatives will be used, as required, in samples for specific analyses according to EPA protocols. The following table summarizes the holding times criteria that will be followed for this project. The holding times and preservation techniques are either those recommended in Title 40 CFR Section 136.3, Table 11, "Required Containers, Preservation Techniques, and Holding Times," or those presented by EPA in Table 3-1 of the *Handbook - Quality Assurance/Quality Control (QA/QC) Procedures for Hazardous Waste Incineration* (EPA-625/6-89-023).

Measurement	Matrix	Preservation ^a	Holding Time ^b
Hexavalent Chromium	1.0N Potassium Hydroxide	Nitrogen gas purge, filter, chill with ice 4°C ± 2°C, final pH ≥ 8.5	14 days to analysis

Notes:

N = Normality

- a CPT samples requiring refrigeration will be preserved on ice from the time of collection through delivery to the analytical laboratory.
- b Holding times are calculated from the date of collection.

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Recommended Quality Measurements for a 3 Run CPT

Analytical Parameter (Analysis)	Sample Name or Type	Total No. of Field Samples	Analytical Procedure Description (Method)	Laboratory QC Measurement Type	Frequency of Applied QC Measurement Type	Total No. of Laboratory QC Measurements	Field QC Measurement Type	Total No. of Field QC Samples	Total No. of Laboratory Analyses ^a
Hexavalent Chromium	Hexavalent Chromium Recirculatory Train Impinger Composite (1.0N Potassium Hydroxide)	3	IC/PCR spectrophotometric detector SW-7199, SW-0061)	MS/MSD	One set per test condition	2	Reagent blank (1.0N potassium hydroxide impinger solution)	1	12
				Field spike	Two per run	6			

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Analytical Quality Control Checks, Frequencies, Target Acceptance Criteria, and Corrective Action

Parameter/Method	QC Check	Frequency	Target Criteria	Corrective Action
Hexavalent Chromium by IC and PCR Spectrophotometric Detector (Method 7199)	Initial Calibration (minimum three (3) standards and one(1) blank)	Daily	Fit of standard curve <ul style="list-style-type: none"> Correlation coefficient ≥ 0.995 	(1) Make necessary adjustments (2) Repeat linearity check
	Initial Calibration Verification (ICV/ICB)	Beginning of analysis sequence	Accuracy as %Recovery <ul style="list-style-type: none"> %Recovery: 90 – 110% 	Repeat calibration
	Continuing Calibration Verification (CCV/CCB)	After every 10 samples	Accuracy as %Recovery <ul style="list-style-type: none"> %Recovery: 90 – 110% 	(1) Repeat initial calibration (2) Reanalyze affected samples
	Laboratory Method Blank	Once per sample batch (maximum 20 samples)	Target Analyte Concentration < RL (05 g/L)	Flag associated sample data
	Laboratory Control Sample/Laboratory Control Sample duplicate (LCS/LCSD)	Once per sample batch (maximum 20 samples) LCSD not required if MSD performed	Accuracy <ul style="list-style-type: none"> %Recovery: 85 – 115% Precision (if applicable) <ul style="list-style-type: none"> RPD $\leq 20\%$ 	(1) Rerun Entire Batch (2) If not rerun, or results are still unacceptable, flag data (3) Discuss in final report
	Matrix Spike/Matrix Spike Duplicate (MS/MSD) analysis	One set per test condition	Accuracy <ul style="list-style-type: none"> %Recovery: 85 – 115% Precision (if applicable) <ul style="list-style-type: none"> RPD $\leq 25\%$ 	Flag data
	Field Spikes	Two per run	Accuracy <ul style="list-style-type: none"> %Recovery: 70 – 130% Precision (if applicable) <ul style="list-style-type: none"> RPD $\leq 35\%$ 	(1) Flag data (2) Discuss results in final report

Summary of Field Quality Control Sample Requirements Comprehensive Performance Test - 3 Runs

Sample ^a	QC Sample Type	Frequency	QC Sample Total
Hexavalent Chromium Train (Method 0061)	Reagent Blanks	One per test condition: 1.0N potassium hydroxide impinger solution	1
	Blank Spikes	One sample spike per test condition	1
	Field Spikes	Two sample spikes per run	6

Summary of Field Quality Control Sample Requirements Comprehensive Performance Test - 3 Runs

Parameter	QC Type	Precision ⁱⁱⁱ	Accuracy ⁱⁱⁱ
Chromium Train (Cr ⁺⁶)			
Hexavalent Chromium Train	Field spikes	≤35% RPD	70 to 130%
Hexavalent Chromium Train	Standard reference material	---	70 to 130% of reference value
Hexavalent Chromium Train	Matrix spikes	≤30% RPD	±25%

ⁱ Precision data quality objectives (DQOs) are defined by relative standard deviation (RSD) or relative percent difference (RPD). See Section 13.0 for the equations used for calculating these precision indicators.

ⁱⁱ The precision criteria should not apply when analytical determinations are near the detection limit of the specific method being performed due to the inherent uncertainty of data determinations derived from trace level samples at or below the method reporting limits. That is, the lower the numbers obtained when applying an analytical method, the greater will be the relative standard deviation of the data. However, in all instances where the criteria have not been met, the data will be flagged, and the acceptance of the data for its intended objectives will be discussed in the final report.

ⁱⁱⁱ Accuracy is, in general, defined as percent recovery of spiked analytes or the bias associated with the measurements of standard reference materials and standards. When standard reference materials are analyzed as accuracy assessment samples, an acceptance range around the "true" value is used to evaluate accuracy.

Method 0061 for Hexavalent Chromium (Cr⁺⁶) in Stack Gas Emissions

Sampling and Field Procedure for Hexavalent Chromium in Stack Gases

Sample Name:	Stack Gas Hexavalent Chromium (Cr ⁺⁶) Train
Sampler:	Stack Sampling Engineer
Process Sample Location:	Stack Sampling Platform
Sampling & Health & Safety Equipment:	<p>Sampling and safety equipment is as follows:</p> <ul style="list-style-type: none">▪ U.S. EPA Hexavalent Chromium (Cr⁺⁶) sampling train, equipped with a peristaltic pump, Teflon[®] fittings and connecting tubes for recirculation▪ Teflon[®] impingers with Teflon[®] connectors▪ 1.0N potassium hydroxide (KOH) impinger solution▪ DI water▪ Silica gel▪ 1-Liter high density polyethylene sample bottles with Teflon[®]-lined lids▪ Nitrogen purge system and nitrogen pressure filtration system▪ Graduated cylinder▪ Safety glasses or face shield▪ Gloves and other safety equipment as required
Sample Collection Frequency:	Continuously for approximately three (3) hours during each sampling run. Sampling volume will be 2 m ³ at a rate not to exceed 0.75 m ³ /hour.
Sampling Procedures:	<p>Train Preparation - Prior to the on-site sample collections, all components of the sampling train and filtration apparatus specifications will be cleaned according to the method specifications. The stack gas sampling collection equipment will be calibrated in accordance with SW-846 Method 0061 and Method 5 standard protocols.</p> <p>The sampling train is assembled as specified in SW-846 Method 0061. The first impinger will be charged with 150 ml of the 1.0 N KOH impinger solution and approximately 75 ml of KOH impinger solution will be placed in the second and third impingers. The fourth impinger will be a stack gas condensate knockout trap and will remain empty. The</p>

fifth impinger will contain indicating silica gel weighed to the nearest 0.5 gram.

Sample Train Operation - An initial traverse is made with a pitot tube at each sample port following U.S. EPA Methods 1 and 2 to establish the stack velocity profile, temperature, and flow rate, and to check for cyclonic air flow. Sample point location will be in accordance with U.S. EPA Method 1. The total sampling time during a run will be approximately 3 hours with a nominal 2 dry standard cubic meters of sample collected. U.S. EPA Method 5 procedures are followed for pre-test and post-test leak checks, isokinetic sampling rate, port changes, and data recording.

Immediately before sample collection, a thorough check of the recirculation system of the first impinger to the probe will be performed and the system will then be started. The KOH recirculating lines will be cooled in an ice bath during sample collection.

Note: The pH of the 1st impinger should be maintained above 8.5 during the entire sampling run. It is highly recommended that the pH be checked at the midpoint of the run for neutralization of the KOH solution. If the pH has dropped below 10, additional KOH should be placed in the 1st impinger.

Cr⁺⁶ Train Sample Recovery - The entire Cr⁺⁶ Train will be removed intact to the cleanup area for sample recovery as follows:

- With the sample train intact and the impinger #4 outlet disconnected from the sampling train, a nitrogen cylinder purge system will be connected to the input of the #1 impinger of the Cr⁺⁶ train. The recirculation line will be capped off. The KOH impingers of the train will then be purged with ultra clean nitrogen gas at a delivery rate of approximately 10 L/min for 30 minutes.
- Impingers #1-#4: The pH of impinger #1 is checked using pH strip paper and recorded on the sample collection sheet. The pH of this solution should be > 8.5. The impinger catches for each impinger (#1 through #4) will be volumetrically measured and combined into a single collection bottle. The glass nozzle, aspirator (or pump), all connecting tubing, and impingers will be rinsed four times using DI water and the rinses will be volumetrically measured and added to the sample bottle.
- The entire impinger train sample will be filtered through a 0.45 µm acetate or Teflon[®] filter in a filtration device equipped with nitrogen pressure connectors. The filtration device will then be washed with DI water and the rinses will be added to the sample. **NOTE: The final volume of the impinger sample with final rinses should be measured and recorded. This volume is required in the**

laboratory to calculate the total Cr⁺⁶ and spike recovery accuracies.

- The silica gel impinger will be weighed to the nearest 0.5 g for determining the amount of moisture gained during sampling.

Quality Assurance:

A 200 ml reagent blank will be collected of the 1.0 N KOH reagent source during one run of the test burn.

Consistent with Section 6.3 of Method 0061, stability of Cr⁺⁶ in the sampling solution will be demonstrated by taking two (2) - 40 mL aliquots of the final Cr⁺⁶ impinger composite and field spiking with Cr⁺⁶ in the following concentrations:

- 10 ppm over the expected concentration
- 25 ppm over the expected concentration

These spikes will be conducted for each run. A blank reagent spike of the 1.0N KOH will also be prepared one time during the test. The parent sample of the aliquots is maintained as the original sample. Each aliquot will be placed in individually numbered sample bottles and submitted for Cr⁺⁶.

The holding times for Cr⁺⁶ samples will be 14 days from collection. All samples should be preserved on ice to 4°C ±2°C. The first impinger of the train will be pH > 8.5 during the test. The impinger may be checked halfway through the test at port change in order to anticipate the adequacy of the KOH strength in finishing the test.

Method References:

Method 0061 – “Determination of Hexavalent Chromium Emissions from Stationary Sources”. Taken from Test Methods for Evaluating Solid Waste, Physical/Chemical Methods. SW-846, Third Edition, September 1986. Final Update I (July 1992), Final Update IIA (August 1993), Final Update II (September 1994), Final Update IIB (January 1995), Final Update III (December 1996), and Final Update IIIA (April 1998). USEPA, OSWER, Washington, D.C. 20460.

Analytical Procedure for Hexavalent Chromium in Stack Gases

Sample Name: 1.0N KOH Probe and Nozzle Rinse, Glassware Rinses, and Impinger Composite Sample

Sample Holding Time: Analyze within 14 days from sample collection.

Sampling Procedures: Samples will be analyzed for Cr⁺⁶ by ion chromatography/post column reactor (IC/PCR) using a spectrophotometric detector (Method 7199). The following procedures will be used during analysis:

Sample Analysis: The samples will be injected into the IC sample loop and introduced to the column. The IC eluent will be a solution of 250 mM (NH₄)₂SO₄/100 mM NH₄OH. The IC will use a guard column (Dionex IonPac NG1) to remove organics followed by a separator column (Dionex IonPac AS7), a high capacity ion-exchange resin column. In the post-column reactor, Cr⁺⁶ is derivatized with a 2 mM diphenylcarbazide/10% methanol solution, forming a colored chromium complex. This colored complex is then quantitated spectrophotometrically at 520 nm using a low volume, flow-through cell equipped with a UV-visible lamp detector. The detector and IC will be connected to an integration unit for data recording.

Data Reporting: The anticipated detection limit of the method is 1 µg/L (ppb). All data will be reported in units of µg/L and will be volumetrically corrected for the original sample volume in the final report.

Method References: Method 0061 - "Determination of Hexavalent Chromium Emissions from Stationary Sources". Taken from Test Methods for Evaluating Solid Waste, Physical/Chemical Methods. SW-846, Third Edition, September 1986. Final Update I (July 1992), Final Update IIA (August 1993), Final Update II (September 1994), Final Update IIB (January 1995), Final Update III (December 1996), and Final Update IIIA (April 1998). USEPA, OSWER, Washington, D.C. 20460.

Method 7199 - "Determination of Hexavalent Chromium in Drinking Water, Groundwater and Industrial wastewater Effluents by Ion Chromatography". Taken from Test Methods for Evaluating Solid Waste, Physical/Chemical Methods. SW-846, Third Edition, September 1986. Final Update I (July 1992), Final Update IIA (August 1993), Final Update II (September 1994), Final Update IIB (January 1995), Final Update III (December 1996), and Final Update IIIA (April 1998). USEPA, OSWER, Washington, D.C. 20460.