Standard Operating Procedure for Determination of Hexavalent Chromium in Ambient Air by Ion Chromatography

MLD039
Revision 5.0

Northern Laboratory Branch
Monitoring and Laboratory Division

Approval Signatures	Approval Date
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Disclaimer: Mention of any trade name or commercial product in this standard operating procedure does not constitute endorsement or recommendation of this product by the California Air Resources Board. Specific brand names and instrument descriptions listed in the standard operating procedure are for equipment used by the California Air Resources Board's laboratory. Any functionally equivalent instrumentation is acceptable.

Table of Contents

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1. Introduction

This standard operating procedure describes the determination of hexavalent chromium (Cr^{+6}) in ambient air samples using ion chromatography (IC). The procedure provides analysis of Cr^{+6} on pre-acid washed, sodium bicarbonate impregnated, ashless, cellulose filters.

2. Summary of Method

Hexavalent chromium is collected on pre-acid washed 37 mm cellulose filters over a 24 hour period. Both sampled and un-sampled filters are stored in a freezer. Sampled filters are later extracted by sonication in 15mL of 20 mM sodium bicarbonate solution for one hour. Filter extract is analyzed by ion chromatography. During analysis, Cr^{+6} exists as a chromate due to the near neutral pH of the eluent. After separation through the column, Cr^{+6} forms a complex with 1,5-diphenylcarbohydrazide which is detected at a wavelength of 530 nm.

3. Acronyms and Definitions

Table I: Acronyms and Definitions

Acronym	Definition
Cr^{+3}	Trivalent Chromium
Cr^{+6}	Hexavalent Chromium
IC	Ion Chromatography
L	Liter
LIMS	Laboratory Information Management System
M	Molar
MDL	Method Detection Limit
mL	Milliliter
MLD	Monitoring and Laboratory Division
mL/min	Milliliters Per Minute
mM	Millimolar

Acronym	Definition
N	Normality
ng/m^3	Nanograms per Cubic Meter
ng/mL	Nanograms per Milliliter
NLB	Northern Laboratory Branch
Nm	Nanometer
QC	Quality Control
QCM	Quality Control Manual
RL	Reporting Limit
RPD	Relative Percent Difference
SDS	Safety Data Sheet
SOP	Standard Operating Procedure
PCR	Post Column Reagent
µL	Microliter

4. Interferences and Troubleshooting

This section outlines the solutions to common instrumentation errors. Please note that this is not a comprehensive list. Reference the instrument manual or contact the manufacturer if this troubleshooting guide does not address nor correct the error.

Table II: Interferences and Troubleshooting

Problem	Possible Solution
Peak Misidentification	In some cases, manual peak integration may be appropriate. Verify sample peak retention times to standard retention times. If there are additional peaks, contamination could have occurred. Additionally, significant retention time differences can signal peak misidentification. Check the age of the guard and analytical columns. See peak retention time drift below.
Cr^{+6} Exceeds Calibration	Perform a dilution and re-run the sample. Initial results determine the appropriate dilution and should target the calibration mid-point.
Peak Retention Time Drift	Changes in flow rate, eluent, and column aging can cause peak retention time drift. Ensure the flow rate is correct. Make new

Problem	Possible Solution
	eluent. If the error persists replace the system columns.
Increased System Pressure	High system pressures signal a blockage in the system (ex:> 3000 psi for a typically 1500 psi set up). Systematically check lines until you find the source of the blockage. For further details reference the instrument operator's manual located in the lab.
Sodium Bicarbonate Interference	High concentrations (> 0.12 M) of sodium bicarbonate may cause flow restrictions during sampling. See section 9.1.4.
Potential Conversion of Cr^{+6} to Cr^{+3}	Post sampled filters should be stored below 4 degrees C. Analyze filters within 21 days of receipt. Store filter extracts in the laboratory refrigerator after extraction. Perform analysis within 24 hours of extraction to minimize conversion.
Post Column Reagent Light and Heat Sensitivity	Exposure to light and heat will cause reagent to degrade and change color. Refrigerate PCR in an opaque polyethylene container to minimize degradation. When properly stored the PCR is stable for one week.

5. Personnel Qualifications and Training

Prior to performing this method, new personnel must be trained by staff with expert knowledge of this method. Personnel must be trained to understand the program's requirements per any applicable State and federal regulations and guidance, and this SOP. Personnel will also be trained on how to safely and properly operate the equipment needed to perform the method, quality assurance components, and LIMS functionality pertaining to the program.

Personnel should provide an initial demonstration of capability prior to performing this method on real-world samples (i.e., data for record). Training will be documented and maintained by the laboratory supervisor.

This SOP assumes familiarity with the operation of Dionex ion chromatography systems. For detailed operation instructions refer to the Dionex operations manual.

6. Safety Requirements

All personnel must follow the general health and safety requirements found in the NLB's Chemical Hygiene Plan.

When preparing solutions, reagents, or handling hazardous materials, wear an appropriate level of personal protective equipment for task being performed. This includes wearing lab coats, protective eyewear, gloves, and utilizing the fume hood. Store acids and flammable materials in the appropriate safety cabinets. See NLB Chemical Hygiene Plan for additional details.

Analyst must read the SDS for all chemicals they use. Analyst should reference additional instrument safety concerns in the safety section of the ion chromatography system operator's manual.

A solution is prepared using concentrated sulfuric acid and thus requires careful attention to the order of mixing to prevent a violent reaction. More details are found in Section 9.1.2.

7. Hazardous Waste

Cr^{+6} analysis generates toxic materials. Dispose of this waste properly. Analyst should keep hazardous waste containers in the laboratory. Hazardous waste collection containers should include secondary containment to protect against leakage or spills. Place one waste container in the fume hood and connect another to each IC instrument to capture waste drainage. Contact the hazardous waste coordinator to obtain hazardous waste labels and verify waste is properly labeled. When containers are roughly ¾ full, contact the hazardous waste coordinator to schedule transfer to the hazardous waste drum. Do not perform waste disposal alone. Transfer the waste slowly to avoid splashes or the drum overflowing.

8. Equipment, Supplies, and Chemicals

8.1. Equipment

8.1.1. Dionex Ion Chromatography (IC) System which includes:

8.1.1.1. Instrument Controller, Gradient Pump, Reagent Delivery Module, Variable Wavelength Detector, and Automated Sampler

8.1.1.2. Operating conditions listed in the table below:

Table III: IC Equipment Components with Operating Conditions

IC Component	Operating Condition
Analytical Column	IonPac AS7
Guard Column	IonPac NG1 or equivalent AG7
Eluent Solution	250 mM Ammonium Sulfate 100 mM Ammonium Hydroxide
Eluent Flow Rate	2mm System - 1.0 mL/min 4mm System – 0.36 mL/min
Post-Column Reagent	2 mM 1,5-Diphenylcarbazide 10% Methanol 0.9 N Sulfuric Acid
Post-Column Flow Rate	2mm System - 0.33 mL/min 4mm System – 0.12 mL/min
Mixing Device	2mm System - 375µL Knitted Reaction Coil 4mm System - 750µL Knitted Reaction Coil
Detector Wavelength	530 nm
Sample Loop Volume	1 mL
Acquisition Software	Chromeleon Chromatography Workstation Software

8.1.2. Additional Equipment

- Refrigerator
- Freezer
- Nanopure Water Filtration System (>18 MΩ-cm)
- Analytical Balance (Annual Calibration)
- Centrifuge
- Sonicator
- Stir Plate with Stir Bar
- Auto-Pipette (Annual Calibration)
- Incubator Oven
- Shaker Table

8.2. Supplies

- Pre-Acid Washed 37 mm Cellulose Filters
- Filter Cassettes
- Chem-Wipes

- Petri Dishes
- Auto-Pipette Disposable Tips
- Filter Drying Racks
- Auto sampler vials
- Weigh Boats
- General Laboratory Glassware
- Wide Mouth Opaque Polyethylene Storage Bottles
- Weighing Spatula
- Hazardous Waste Containers
- 1 L Teflon bottle
- Disposable Gloves
- 30 mL polypropylene vessels
- Plastic forceps
- Ziploc bags
- Sonicator racks

8.3. Chemicals: All chemicals must be spectrophotometric grade

- Nanopure Water (>18 MΩ-cm) CAS# 7732-18-5
- Ammonium Sulfate (Reagent Grade) CAS# 7783-20-2
- Ammonium Hydroxide 29% (Reagent Grade) CAS# 1336-21-6
- 1,5-Diphenylcarbazide (Reagent Grade) CAS# 140-22-7
- Methanol (Reagent Grade) CAS# 67-56-1
- Sulfuric Acid 98% (Reagent Grade) CAS# 7664-93-9
- Sodium Bicarbonate (Reagent Grade) CAS# 144-55-8
- Ultra High Purity Helium (Reagent Grade) CAS# 7440-59-7
- NIST-traceable Cr^{+6} Standards 1000 µg/mL in water CAS# 18540-29-9

9. Procedures

9.1. Preparation of Solutions and Reagents:

Record preparation of solutions and reagents with chemical names, concentrations, dates, and chemist initials in the laboratory notebook and on any holding containers.

9.1.1. Prepare the Eluent at a final concentration of:

- 250 mM Ammonium Sulfate and
- 100 mM Ammonium Hydroxide

In a 2 L polyethylene bottle, dissolve 66.0 g of ammonium sulfate in 1 L of nanopure water. Add 13.0 mL of 29% ammonium hydroxide. Dilute to 2.0 L with nanopure water.

Note: Eluent solution must be re-made if not used within 3 months.

9.1.2. Prepare the Post Column Reagent (PCR) at a final concentration of:

- 2 mM 1,5-Diphenylcarbazide
- 10% Methanol
- 0.9 N Sulfuric Acid

Add 0.5 g of 1,5-Diphenylcarbazide to a 1 L volumetric flask. Add 100 mL of Methanol. Stir until all 1,5-Diphenylcarbazide is dissolved. Once dissolved, add approximately 250 mL of nanopure water. In a separate 1000 mL beaker, filled with 500 mL nanopure water*, add 25 mL of 98% sulfuric acid ***slowly***. Once the nanopure water sulfuric acid solution has cooled to room temperature, carefully pour the solution into the 1 L volumetric flask with the 1,5-Diphenylcarbazide, methanol, nanopure water solution. Bring the solution to a volume of 1L with nanopure water. Label solution with the date prepared and chemist initials.

***Warning: Adding 25mL sulfuric acid before adding 500 mL nanopure water will cause a dangerous reaction. Ensure 500 mL nanopure water is added prior to 25 mL sulfuric acid. DO NOT ADD SULFURIC ACID DIRECTLY INTO THE DPC/METHANOL MIXTURE AS IT WILL REACT VIOLENTLY.**

Note: Refrigerate PCR in an opaque polyethylene container due to light and heat sensitivity. When properly stored the PCR is stable for one week. Discard unused PCR weekly in the hazardous waste container. Prepare fresh PCR as needed. Label solution with the date prepared and chemist initials.

9.1.3. Prepare Hexavalent Chromium Standards

Prepare working standards and controls of hexavalent chromium from a NIST traceable stock. Prepare solutions every two weeks and store in a refrigerator. Bring solutions to room temperature prior to analysis. Table IV directs the preparation of Cr^{+6} standards in appropriately labeled volumetric flasks. Label solution with the date prepared, target concentration, and chemist initials.

Do not use stock or substock solutions past the manufacturer expiration date. Store stock, substock, and standard solution in the refrigerator unless they are in use.

Table IV: Hexavalent Chromium Standards

Standards	Target Concentration	Preparation
Stock	1000 µg/mL in water	Prepared by Vendor & NIST Traceable
Substock 1	10 µg/mL	Add 500 µL of stock. Bring to 50 mL volume using 20 mM sodium bicarbonate solution.
Substock 2	0.10 µg/mL	Add 500 µL of substock 1. Bring to 50 mL using 20 mM sodium bicarbonate solution.
Standard 1	0.05 ng/mL	Add 50 µL of substock 2. Bring to 100 mL using 20 mM sodium bicarbonate solution.
Standard 2	0.10 ng/mL	Add 100 µL of substock 2. Bring to 100 mL using 20 mM sodium bicarbonate solution.
Standard 3	0.50 ng/mL	Add 500 µL of substock 2. Bring to 100 mL using 20 mM sodium bicarbonate solution.
Standard 4	1.0 ng/mL	Add 1000 µL of substock 2. Bring to 100 mL using 20 mM sodium bicarbonate solution.
Standard 5	1.5 ng/mL	Add 1500 µL of substock 2. Bring to 100 mL using 20 mM sodium bicarbonate solution.
Standard 6	2.0 ng/mL	Add 2000 µL of substock 2. Bring to 100 mL using 20 mM sodium bicarbonate solution.
Control	1.0 ng/mL	Add 1000 µL of substock 2 Control. Bring to 100 mL using 20 mM sodium bicarbonate solution. *Note: Control is prepared from a separate source or has a different lot number.*

Standards	Target Concentration	Preparation
Spike	1.0 µg/mL	Add 2500 µL of substock 1. Bring to 25 mL using 20 mM sodium bicarbonate solution.

9.1.4. Prepare Sodium Bicarbonate Filter Impregnating Solution at a final concentration of 0.12 M:

In a 500 mL polyethylene storage bottle, dissolve 5.0 g of sodium bicarbonate in nanopure water. Bring to 500mL volume using nanopure water. Once dissolved, store the sodium bicarbonate solution in the laboratory refrigerator for up to one week. Record the solution concentration, date of sodium bicarbonate preparation, filter impregnation, filter manufacturer, lot number, and chemist initials in the laboratory notebook. Sodium bicarbonate solution can be disposed of in the lab sink.

9.1.5. Prepare Sodium Bicarbonate Extract Solution at a final concentration of 20 mM:

In a 500 mL polyethylene storage bottle, dissolve 0.84 g of sodium bicarbonate in nanopure water. Bring to 500mL volume using nanopure water. Once dissolved, store the sodium bicarbonate solution in the laboratory refrigerator for up to one week. Record the solution concentration, date of sodium bicarbonate preparation, and chemist initials in the laboratory notebook. Sodium bicarbonate solution can be disposed of in the lab sink.

9.2. Filter Preparation and Inspection

9.2.1. Filter Inspection

Inspect filters for structural abnormalities. Reject filters containing dents, tears, pinholes, discoloration, thin spots, or any other visible abnormalities.

9.2.2. Sodium Bicarbonate Impregnation of Cellulose Filters

Prepare enough filters for upcoming mail-outs, but not more than 100 per batch. Add pre-acid washed cellulose filters to a 0.12 M sodium bicarbonate filter impregnating solution in a clean 1L Teflon bottle. Add enough solution to saturate filters and soak them over night on a shaker table at low speed. Remove saturated filters with forceps and place on the drying rack, in a single layer.

Place single layered filters on the drying rack in the incubator oven until dried. Set the incubator oven to 40 degrees C. Once filters are dry, immediately place them in a clean Ziploc bag and store in the freezer. Label the bag with the preparation date and preparer's initials.

9.2.3. Filter Acceptance Testing

Extract and analyze three percent of prepared filters per batch of sodium bicarbonate impregnation. Results must be below the reporting limit. If results are above or equal to the reporting limit, perform a reanalysis. If results are still above or equal to the reporting limit, discard the batch. See Table VI. Quality Control Criteria.

9.2.4. Filter Storage and Mail Out

For filters that have passed filter acceptance test, place individual impregnated filters in filter cassettes, and place them in individual petri dishes. Prepare enough filters for scheduled mail out. Use the remaining filters as blanks when analyzing post sampled filters. Store any un-sampled filters in the freezer for up to two years. Discard un-sampled filters that exceed two year holding times.

9.2.5. Post-Sampled Filter Handling

Samples should be received from the field at less than 4°C. Flag samples received at > 4°C. Store samples received from the field in original containers in the laboratory freezer below 4°C. Record the freezer temperature on the freezer temperature log each time filters are removed from or added to freezer. Flag samples if temperatures exceed 4°C. Analyze post-sampled filters within 21 days of receipt. Flag samples with holding times exceeding 21 days.

9.3. Filter Extraction

Due to chemical reduction, there is a potential for the conversion of Cr^{+6} to Cr^{+3}. Store filter extracts in the laboratory refrigerator after extraction. Perform analysis within 24 hours of extraction to minimize conversion. See section 9.4.1. Chemist must ensure that the IC is functioning properly prior to extracting filters. Prior to extraction, perform an instrument calibration to ensure that the instrument obtains an acceptable calibration correlation coefficient of $r \geq 0.980$ (See Table VI. Quality Control Criteria). If acceptable, proceed with the extraction. Mandatory quality control (QC) samples are

located in Table V. QC samples are made using the same reagents and media.

Table V. Quality Control Samples

QC Sample	Target Concentration	Preparation
Extraction Solution Blank	< RL	Add 15 mL of extraction 20 mM sodium bicarbonate solution to a polypropylene vessel.
Filter Blank	< RL	Add 15 mL of extraction 20 mM sodium bicarbonate solution and an un-sampled filter to a polypropylene vessel.
Spike	1 ng/mL	In a polypropylene vessel, place an un-sampled filter. Add 15 µL of 1.0 µg/mL Cr^{+6} spike solution to un-sampled filter, and allow it to dry. Then add 15 mL of extraction 20 mM sodium bicarbonate solution to the polypropylene vessel.

Individually remove filters from original petri dishes. Remove filters by decoupling filter cassettes and carefully place filters in individually labeled polypropylene vessels. Add 15 mL of 20 mM sodium bicarbonate extraction solution to each vessel. Place vessels with samples in a sonicator in the sonication rack. Add tap water to the sonication tub. Ensure the tap water level does not reach the lids of the vessels. Sonicate samples for one hour.

9.4. Analysis

The sample analysis process includes preparing extracts for analysis, loading the auto-sampler, and ensuring the integrity of the results.

9.4.1. Preparing Extracts for Analysis

Once filter sonication is complete, turn off the sonicator, and drain the sonication tub by opening the water valve. Remove the vessels containing the extracts. One sample at a time, carefully homogenize the sample by gently shaking, remove the vessel lid, and transfer approximately 5mL of each extract (enough needed

for analysis) to individually labeled auto sampler vials, appropriate to the IC instrument used for analysis. Analyze samples within 24 hours of extraction. Flag extracted samples not analyzed within 24 hours.

9.4.2. Operating the IC

Program the instrument controller with the sample sequence and appropriate QC (see section 10). A system flush, which consists of water, should be done in the beginning and end of the analytical run sequence to rinse out the IC. See example of recommended analytical run sequence below.

- System Flush
- Calibration Standard(s)
- Control
- Check Standard
- Filter Blank
- Extraction Solution Blank
- Spike
- Check Standard
- Set of Samples (up to 9 samples)
- Sample Replicate
- Check Standard
- System Flush

Load samples into the auto-sampler ensuring that their location matches the run sequence. Ensure proper function of the IC by confirming that QC meets requirements found in section 10. For detailed instrument operating instructions, refer to the Dionex operations manual.

10. Quality Control

Quality control measures include a six point calibration curve, secondary source controls, check standards, filter blanks, extraction solution blanks, and spikes that must be performed with each analysis. Furthermore, an annual method detection limit verification must be completed.

Table VI. Quality Control Criteria

QC	Acceptance Criteria	Frequency	Corrective Action
Calibration	Calibration correlation coefficient r must be ≥ 0.980	One per analytical sequence.	Prepare new standards and re-run the analysis.
Check Standard	Check standard must ± 20% of the target concentration of 1 ng/mL.	Beginning and end of each analytical run sequence. After every 10 samples, at least.	If the check standard is outside the criteria limit, take action to bring the system back into control and repeat the analysis. Samples must be bracketed by successful checks standards. If a check standard is still outside the criteria limit, and there is no sample extract remaining for re-analysis, the results are invalid.

QC	Acceptance Criteria	Frequency	Corrective Action
Control	Control is prepared from a secondary source and analyzed at a target concentration of 1ng/mL. The initial warning and control limits are set at ±8 and ±10 Percent Difference (PD) respectively from the target value. Once a minimum of 20 control standard results are obtained, the limits for tolerance of the control results around the mean should be set as follows (See the QCM for additional details): • Upper Control Limit = Mean + 3 Standard Deviations • Upper Warning Limit = Mean + 2 Standard Deviations • Lower Warning Limit = Mean - 2 Standard Deviations • Lower Control Limit = Mean - 3 Standard Deviations	One per analytical run sequence.	If the control standard is outside the control limit, take action to bring the system back into control and repeat the entire analysis. If control is still outside the criteria limit, and there is no sample extract remaining for re-analysis, the results are invalid.
Spike	Blank filters are spiked with a target concentration of 1 ng/mL. The spike recovery limit is $\pm$ 20% from the target concentration.	One per analytical run sequence.	If the spike fails, repeat the entire analysis. The spike cannot be re-prepared because it is QC for the extraction. If the spike is still outside the criteria limit, and there is no sample extract remaining for re-analysis, the results are invalid.

QC	Acceptance Criteria	Frequency	Corrective Action
Filter Acceptance Testing	Extract and analyze three percent of randomly selected prepared filters. For example, if 1 box of 100 filters are prepared with sodium bicarbonate impregnation, extract and analyze 3 filters. Hexavalent chromium results must be < RL.	Upon completion of sodium impregnation for each batch of filters.	If hexavalent chromium levels are ≥ the RL, perform a reanalysis. If results are still ≥ the RL, discard the entire batch and start again. If the problem persists, notify the section manager and contact the manufacturer. No filters are to be used until they pass filter acceptance testing requirements.
Filter Blank	Filter blank levels of Cr^{+6} must be < the RL.	One per analytical run sequence.	If the filter blank fails, repeat the entire analysis. The blank cannot be re-extracted because it is QC for the extraction. If the filter blank is still outside the criteria limit, and there is no sample extract remaining for re-analysis, the results are invalid, unless they are ≥ 10 times the Filter Blank result.

QC	Acceptance Criteria	Frequency	Corrective Action
Extraction Solution Blank	Extraction solution blank levels of Cr^{+6} must be < the RL.	One per analytical run sequence.	If the extraction solution blank fails, repeat the entire analysis. The blank cannot be re-extracted because it is QC for the extraction. If the extraction solution blank is still outside the criteria limit, and there is no sample extract remaining for re-analysis, the results are invalid, unless they are ≥ 10 times the Extraction Solution Blank result.
Replicate	Replicates must be < 20 RPD.	After every ninth sample, at least. All sample runs must contain a replicate.	If the replicate is ≥ 20 RPD and ≥ five times the RL, the analytical run sequence must be performed again. If replicates are still outside the criteria limit, and/or there is no sample extract remaining for re-analysis, the results are invalid.
Annual Verification MDL	A passing MDL verification requires a valid calibration, check standards, control, spike, extraction solution blank, filter blank, and meet the specified criteria in the QCM.	Annually	If the MDL acceptance criteria is not met, repeat the entire analysis. If the criteria is still not met, prepare MDL spikes at a different concentration to re-calculate a new MDL. Repeat these steps until the MDL acceptance criteria is met.

QC	Acceptance Criteria	Frequency	Corrective Action
Reporting Limit	Reporting limits (RL) should be verified annually and meet the following criteria: • RL is ≥ the LOQ. • RL should be ≥ the lowest calibration standard. See QCM for additional details.	Annually	During the annual verification procedure, if the RL is < the LOQ, then the RL should be raised to an appropriate limit. If the RL is > two times the LOQ, then consideration should be given to lower the RL.
Filter QC	• Sampled filters should be received from the field < 4°C. • Prior to extraction, store filters in the laboratory freezer < 4°C.	Every filter	• Flag samples received > 4°C. • Flag stored filters if temperatures exceed 4°C.
Filter Extract QC	• After extraction, store filter extracts in the laboratory refrigerator < 8°C. • Analyze post-sampled filters within 21 days of receipt. • Analyze filters within 24 hours of extraction.	Every filter	• Flag stored filter extracts if temperatures exceed 8°C. • Flag samples with holding times exceeding 21 days. • Flag samples not analyzed within 24 hours of extraction.

11. Sample and Data Management

Data management consists of samples logged into the Laboratory Information Management System (LIMS), documentation of unusual occurrences and their resolutions, creation of data packages (monthly, amendments, and special projects) for peer review and management approval, submittal of data to clients, and archival procedures for sample media and respective chains of custody. Program and maintenance notebooks and/or logbooks are to be kept with the instrumentation at all

times. Sample extraction, sample analysis, calibration correlation coefficient r, average retention times, eluent preparation, post-column-reagent preparation, standard preparation, current equipment, and instrument changes are recorded in the laboratory notebook.

11.1. After samples are analyzed, review and document the sample run. Review all calibration curves, chromatograms, and associated QC prior to transferring the data to LIMS. Add the LIMS generated transfer summary report to the documentation. Maintain these records for five years, plus the current year.

11.2. Data packages undergo a multi-level data validation process. This process includes analyst review, peer review, and laboratory management review and approval in line with the QCM. Data packages created by the analyst must consist of the following:

11.2.1. Documentation of the method and program name, standards expiration dates, MDL verification dates, criteria limits, anomalies, and comments for special projects.

11.2.2. Summary of the data generated for a sample date period.

11.2.3. Summary of QC data, analytical run sequence information, calibration curves, and any additional QC documentation of interest.

12. Calculations

12.1. Spiked Samples

$$Spike\ Percent\ Recovery\ = \frac{Spike\ Result}{Spike\ Target\ Concentration} \times 100$$

12.2. Replicate

$$Replicate\ Relative\ Percent\ Difference = \frac{|Result - Replicate|}{((Result + Replicate) \div 2)} \times\ 100$$

12.3. Conversion of Aqueous Units to Aerometric Units

Cr^{+6} is analyzed in an aqueous solution (ng/mL). This value can be converted to aerometric units (ng/m^3). The conversion is calculated using the formula below:

$$Cr^{+6}\ \frac{ng}{m^3} = \frac{Extraction\ Volume\ mL\ \times \left[Cr^{+6}\ \frac{ng}{mL}\right]}{Sampler\ Volume\ m^3}$$

13. Revision History

	Date	Updated Revision	Original Procedure
1	**Description: SOP MLD039 Revision Number unknown**		
	Approval Date: March 1995	Note: Revisions were not recorded.	
2	**Description: SOP MLD039 3.0**		
	Approval Date: March 21, 2002	Note: Revisions were not recorded.	
3	**Description: SOP MLD039 4.0 Method Change**		
	Approval Date: May 17, 2018	Method Change: • Analytical Column AS7 • Guard Column NG1 • PCR Rate 0.33 mL/min • New Eluent Solution • Acid Washed Filters • 750 µL Reaction Coil • 5 Point Calibration • Detector Wavelength 530nm	Prior Method: • Analytical Column CS5 • Guard Column CG5 • PCR Flow 0.50 mL/min • Old Eluent Solution • Non-Acid Washed Filters • 400 µL Reaction Coil • 4 Point Calibration • Detector Wavelength 520nm
4	**Description: SOP MLD039 4.0 Addendum A31 Method Improvements**		

	Approval Date: November 7, 2019	Method Improvements: • 6 Point Calibration • IonPac NG1 or equivalent AG7 • Correction: 0.12 M sodium bicarbonate • Filter preparation process to include sodium bicarb overnight treatment and incubator drying. • Sampled filters are extracted by sonication in 15mL of 20 mM sodium bicarbonate solution for one hour. • Filter extraction using 30 mL polypropylene vessels. • Substocks, Standards, Control, Blanks, and Spike made using 20 mM sodium bicarbonate solution. • Mixing Device: 2mm System - 375µL Knitted Reaction Coil 4mm System - 750µL Knitted Reaction Coil • Correction: PCR: 0.9 N sulfuric acid • PCR Flow Rate: 2mm System - 0.33 mL/min 4mm System – 0.12 mL/min • Eluent Flow Rate:	Prior Method: • 5 Point Calibration • Guard Column NG1 • 0.12 mM sodium bicarbonate • Filter preparation process of air drying and chem-wipes. • Sampled filters are extracted by sonication in 15mL of nanopure water for three hours. • Filter extraction using 50 mL glass weighing bottles. • Substocks, Standards, Control, Blanks, and Spike made using nanopure water. • Mixing Device: 4mm System - 750µL Knitted Reaction Coil • PCR: 1 N sulfuric acid • PCR Flow Rate: 2mm System - 0.33 mL/min • Eluent Flow Rate: 2mm System - 1.0 mL/min

		2mm System - 1.0 mL/min 4mm System – 0.36 mL/min	
5	**Description: SOP MLD039 5.0**		
	Approval Date: October 25, 2021	Changes: • Samples should be received from the field less than 4° C. • Filter acceptance testing	Prior: • No receipt temperature requirements. • Filter acceptance testing

14. References

14.1. Dionex Application Update 144: Determination of Hexavalent Chromium in Drinking Water Using Ion Chromatography, 2003. http://tools.thermofisher.com/content/sfs/brochures/4242-AU144_LPN1495.pdf

14.2. South Coast Quality Management District Standard Operating Procedure 0046: The Analysis of Hexavalent Chromium in Ambient Air by Ion Chromatography, July 26, 2017.

14.3. Monitoring and Laboratory Division Laboratory Quality Control Manual, Revision number 4.0, September 17, 2018. https://www.arb.ca.gov/aaqm/sop/nlbqcm.pdf.

14.4. Final Chemical Hygiene Plan for Northern Laboratory Branch 1927 13th Street, 1900 14th Street, June 2019 or current.

14.5. California Air Resources Board SOP MLD076, Revision 0.0: Standard Operating Procedure for Preparation of Northern Laboratory Branch's Standard Operating Procedures, July, 2017.

14.6. California Air Resources Board SOP MLD038: Standard Operating Procedure for Hazardous Waste Management, June, 2017.

14.7. Thermo Fisher Scientific Chromeleon Chromatography Data System, Version 7.3 or later.