

South Coast Air Quality Management District
Science and Technology Advancement

Monitoring and Analysis Division
Laboratory Services Branch



STANDARD OPERATING PROCEDURE

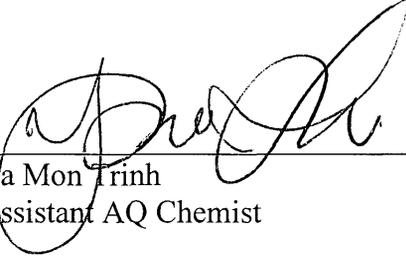
FOR

**THE ANALYSIS OF HEXAVALENT CHROMIUM IN
AMBIENT AIR BY ION CHROMATOGRAPHY**

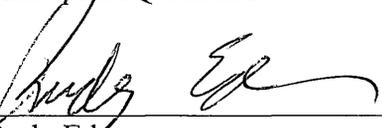
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PREPARATION, REVIEWS AND APPROVALS

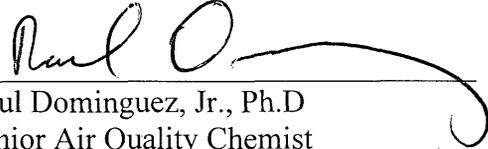
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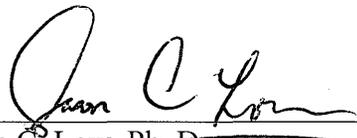
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REVISION HISTORY

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March 5, 2010

REVISION CHANGES FROM PREVIOUS VERSION

STANDARD OPERATING PROCEDURE FOR THE ANALYSIS OF HEXAVALENT CHROMIUM IN AMBIENT AIR BY ION CHROMATOGRAPHY

Section	Revisions
1.0	Previously Section 1.0 & 2.0 - Combined sections
3.0	Previously Section 4.0 - New instrument, equipment, and operating conditions
4.0	Previously Section 5.0 - Modified and added to the list of chemicals and materials
5.0	Previously Section 6.0 - Modified procedure
6.0	Previously Section 7.0 - Modified procedure
7.0	Previously Section 8.0 - Changed format - Added subsections

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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 South Coast Air Quality Management District. Specific brand names and instrument descriptions listed in the Standard Operating Procedure are for equipment used by the South Coast Air Quality Management District laboratory. Any functionally equivalent instrumentation can be used.

1.0 INTRODUCTION

1.1 History

The California Air Resources Board identified hexavalent chromium (Cr^{+6}) as a toxic air contaminant in January 1986. Chromium is a natural constituent of the earth's crust and present in several oxidation states. Trivalent chromium (Cr^{+3}) is naturally occurring, environmentally pervasive and a trace element in man and animals. Hexavalent chromium is anthropogenic from a number of commercial and industrial sources. It readily penetrates biological membranes and has been identified as an industrial toxic and cancer causing substance. Hexavalent chromium is a known inhalation irritant and is associated with respiratory cancer. Exposure is primarily associated with chrome plating and the anodizing process, cement kiln operations, and emissions from chromate treated cooling towers.

Hexavalent chromium has been measured in ambient air at sites located throughout California including the South Coast Air Basin. The AQMD measures hexavalent chromium by drawing ambient air through cellulose filters impregnated with sodium bicarbonate using a Xontech® 920 toxic air sampler. To achieve the lower detection limits needed for some measurement requirements, filters are composited, analyzed and reported as a group. The analysis procedure for hexavalent chromium deposited on 37mm and 47mm cellulose filters are described in this document.

1.2 Method Summary

This method is used to determine the amount of Cr^{+6} in ambient air by analyzing the deposits on sodium bicarbonate impregnated ashless cellulose filters, which are submitted to the laboratory by site operators. The filters are extracted in de-ionized water via sonication for three hours and then filtered. The extract is analyzed by ion chromatography using a system comprised of a guard column, analytical column, a post-column derivatization module, and a UV-Vis detector. In the analysis procedure, Cr^{+6} exists as chromate due to the near neutral or basic pH of the eluent. After separation through the column, hexavalent chromium forms a complex with diphenylcarbazide

(DPC) which is detected at a wavelength of 530 nm. The peak analysis is determined using Dionex Chromeleon® software, version 6.8. This method is based on a modification of the California Air Resources Board Hexavalent Chromium in Ambient Air Method CARB MLD-039.

2.0 INTERFERENCES

2.1 Sodium Carbonate

High levels of sodium carbonate in the sample may cause interferences with the analysis

2.2 Sodium Bicarbonate

Higher concentrations of sodium bicarbonate impregnating solution may cause flow restrictions during ambient air sampling. Trace amounts of hexavalent chromium may be present in filters impregnated with sodium bicarbonate solution. The hexavalent chromium concentration in the impregnated filters should be less than 50 ppt.

2.3 Filter Pore Size

The use of smaller pore size impregnated filter has been shown to cause restrictions during sampling. Sampling details are presented in SOP00052 Standard Operating Procedure for Xontech® 920.

3.0 INSTRUMENT AND EQUIPMENT

3.1 Dionex Ion Chromatographic System Modular Units:

- Gradient pump (ICS-3000 SP-1)
- Reagent Delivery Module (ICS-3000 TC-1)
- UV/Vis Detector (ICS Series VWD-1)
- Automated Sampler (AS-1) - controlled directly from the Chromeleon® workstation

This SOP assumes familiarity with the installation and operation of the Dionex ion chromatographic system as specified above and Chromelon® software. For detailed instructions in the operation of the Dionex ion chromatograph (IC), refer to the Dionex operations manual.

3.2 IC Operating Conditions:

Sample loop volume: 1 mL

Analytical column	Dionex, Ion Pac AS7 or equivalent
Guard column	Dionex Ion Pac AG7 or equivalent
Eluent solution	333 mM Ammonium sulfate ((NH ₄) ₂ SO ₄) 140 mM Ammonium hydroxide
Eluent flow rate	1.0 ml/min
Post-column reagent	2mM Diphenylcarbazide (DPC) 10% Methanol 1.8N Sulfuric acid
Post-column flow rate	0.35 mL/min
Mixing device	Reaction coil
Detector wavelength	530 nm
Acquisition Software	Dionex Chromeleon®, version 6.8

4.0 MATERIALS AND CHEMICALS

4.1 Materials

- Chain of custody
- 37mm and 47mm diameter cellulose filters
- Black filter ring holders (37mm) and blue ring filter holders (47mm)
- Plastic Petri dishes, large enough to hold a 37mm filter
- Volumetric flask: 100 mL, 500 mL, 1 L
- Wide-mouth polyethylene storage bottles: 1L
- Sartorius GMBH Gottingen analytical balance (Type: A-120-9)
- Pipettor with disposable pipette tips: 100-1000 µL and 1-10 mL
- 30 mL Teflon® tubes
- Ultrasonic bath
- Large glass Petri dish
- UHP helium or UHP nitrogen
- Graduated cylinders: 25 mL, 100 mL
- Dionex vials for samples (10 mL)
- Eluent/post-column reagent filtering apparatus (0.22 µm GSWP filters, 300 mL filtering glass funnel, aluminum clamp, glass support base with silicone stopper, vacuum pump)
- Sample filtering apparatus (20 mL disposable syringes, 0.22 µm hydrophilic polyethersulfone (PES) filters)
- 50 mL polypropylene centrifuge tubes

- pH strips

4.2 Chemicals: All chemicals are at least ACS grade

- Ammonium sulfate ($(\text{NH}_4)_2\text{SO}_4$)
- 1,5- diphenylcarbazine (DPC)
- Methanol (CH_3OH)
- Sulfuric acid (H_2SO_4)
- Sodium bicarbonate (NaHCO_3)
- Ammonium Hydroxide ($\text{NH}_3 \cdot \text{H}_2\text{O}$)
- ASTM Type 1 deionized water ($>18 \text{ M}\Omega\text{-cm}$)
- Hexavalent chromium stock standards (National Institute of Science and Technology (NIST) certified). Two stock solutions are purchased, one for making working standards, the other for making a working control. The two solutions are from either different lot numbers or different companies.)

5.0 PREPARATION OF ELUENT

5.1 Eluent

Stock eluent is prepared by dissolving 66.0 g of $(\text{NH}_4)_2\text{SO}_4$ in 500 mL of deionized water. After $(\text{NH}_4)_2\text{SO}_4$ is completely dissolved, the volume is brought up to 1 L using 18 $\text{M}\Omega\text{-cm}$ deionized water. The solution is filtered using the filtering apparatus and a 0.22 μm GSWP filter. In a 500 mL volumetric flask, 14 mL $\text{NH}_3 \cdot \text{H}_2\text{O}$ is diluted to the mark on the flask with deionized water. The $\text{NH}_3 \cdot \text{H}_2\text{O}$ and the filtered $(\text{NH}_4)_2\text{SO}_4$ solutions are combined to make 1.5 L of solution. The final concentrations of ammonium sulfate and ammonium hydroxide are 0.333M and 0.140M, respectively. Working eluent is generated by the Dionex gradient pump which performs a 1:1 mixing of stock eluent with deionized water.

6.0 PREPARATION OF POST-COLUMN REAGENT

6.1 Post-Column Reagent

This solution is light sensitive and needs to be prepared daily as needed. Weigh 0.5g of DPC in a weighing boat and transfer to a 1 L volumetric flask. Add 100 mL of HPLC grade methanol. Rinse the weighing boat with a portion of the 100 mL methanol into the 1 L volumetric flask. When all DPC has dissolved, add about 500 ml of deionized water, then 50ml of 96% ACS grade sulfuric acid. Bring the solution to volume with deionized water. Filter the solution using the filtering apparatus and a 0.22 μm GSWP filter.

Transfer the post-column reagent to a wide-mouth 1 L bottle. This bottle is placed in the post-column reagent delivery module on the IC.

7.0 PREPARATION OF HEXAVALENT CHROMIUM STANDARDS, CONTROLS, AND SPIKE SOLUTION

These solutions are prepared weekly and are stored in the refrigerator (LAB 6) at approximately 4°C. Both hexavalent chromium calibration and control stocks are NIST traceable. Hexavalent chromium stocks are usually acquired in 1000 ppm concentrations. All standards are stored in the refrigerator at approximately 4°C until ready for use. The solutions are brought to room temperature for an hour prior to analysis.

7.1 Calibration Standards

Dilute 100 µL of 1000 ppm Cr⁺⁶ stock to 100 ml using deionized water to make a 1 ppm Cr⁺⁶ solution. Dilute 500 µL of 1 ppm Cr⁺⁶ sub-stock to 100 mL using deionized water to make a 5000 ppt Cr⁺⁶ calibration working stock solution. Transfer a portion of this solution to a 50 mL polypropylene centrifuge tube.

Target Cr ⁺⁶ Concentration	Standard	Volume standard solution	Final Volume
50 ppt	5000 ppt	1 mL	100 mL
100 ppt	5000 ppt	2 mL	100 mL
250 ppt	5000 ppt	5 mL	100 mL
500 ppt	5000 ppt	10 mL	100 mL
1000 ppt	5000 ppt	20 mL	100 mL

7.2 Check Standards

Dilute 100 µL of 1000 ppm Cr⁺⁶ stock to 100 ml using deionized water to make a 1 ppm Cr⁺⁶ solution. Dilute 500 µL of 1 ppm Cr⁺⁶ sub-stock to 100 mL using deionized water to make a 5000 ppt Cr⁺⁶ calibration working stock solution. Transfer a portion of this solution to a 50 mL polypropylene centrifuge tube.

Target Cr ⁺⁶ Concentration	Standard	Volume standard solution	Final Volume
100 ppt	5000 ppt	2 mL	100 mL
500 ppt	5000 ppt	10 mL	100 mL

7.3 Control Standards

Dilute 1000 µL of 100 ppm Cr⁺⁶ stock to 100 ml using deionized water to make a 1 ppm Cr⁺⁶ solution. Dilute 500 µL of 1 ppm Cr⁺⁶ sub-stock to 100 mL using deionized water to make a 5000 ppt Cr⁺⁶ calibration working stock solution. Transfer a portion of this solution to a 50 mL polypropylene centrifuge tube.

Target Cr ⁺⁶ Concentration	Standard	Volume standard solution	Final Volume
250 ppt	5000 ppt	5 mL	100 mL
1000 ppt	5000 ppt	20 mL	100 mL

7.4 Spike Solution

Dilute 1 mL of 1 ppm Cr⁺⁶ control standard solution with 49 mL deionized water in a 50 mL polypropylene centrifuge tube to make a 20 ppb spike solution.

8.0 PREPARATION OF FILTERS FOR HEXAVALENT CHROMIUM SAMPLING

8.1 Initial Filter Acceptance Test

10 filters are selected randomly from newly ordered batches of filters. The filters are extracted with 15 mL of DI water and sonicated for 3 hours. The solutions are filtered and the extracts are analyzed. The hexavalent chromium values must be below LOD (20 ppt). The filters are discarded if they are above the LOD. If they are below the LOD, the filters are impregnated with sodium bicarbonate.

8.2 Preparation of 0.12M Sodium Bicarbonate Impregnating Solution

Weigh 5.0g of sodium bicarbonate in a weighing boat and transfer to a 500 mL volumetric flask. Rinse the weighing boat with DI water into the flask. Add DI water to the mark while swirling the contents until dissolved.

8.3 Impregnation of Cellulose Filters

Cellulose filters (37mm and/or 47mm) are handled with clean gloves and Teflon®-coated forceps during this process. Put approximately 50 pieces of cellulose filters into a clean wide mouth Teflon® bottle. Pour freshly prepared 0.12M sodium bicarbonate solution into the bottle until it covers the topmost filter. Cover the bottle with a Teflon® lid and

allow filters to soak for at least 30 minutes while agitating gently on a shaker.

8.4 Preparation of Suction Filtration System

Meanwhile, prepare a clean 56-mm porcelain Büchner filter funnel. Cut a clean quartz filter to fit the diameter dimension of the Büchner filter funnel, place on the perforated plate of the funnel, and dampen the filter with deionized water. Attach the funnel on the top of a filtering flask equipped with a one-hole rubber stopper and hose connector. After soaking, place about 25 filters on the Büchner funnel. Cover the funnel with parafilm, connect the hose connector to the vacuum pump and begin suction filtration. Repeat this process until all filters have been filtered.

8.5 Drying of Impregnated Filters

Spread the filters on clean glass plates, and place inside a vacuum oven. The vacuum oven is purged with UHP nitrogen gas. Dry the filters in a vacuum oven for at least 30 minutes or until filters are dry.

8.6 Light Inspection

After impregnation, the filters are inspected for any tears, holes, or contamination as per SOP 00102 "Standard Operating Procedure for Visual Inspection & Acceptance of Cellulose Fiber Filters." The accepted filters are placed in a Ziploc® bag. The bag is labeled with the light inspection date, type of filter, impregnating solution, filter lot number, and initial of light inspector. Place rejected filters in a separate bag, which is also labeled similarly to the accepted filters, but identified as rejects. The bags are stored in a refrigerator (LAB 4) at approximately 4°C. The filters are retained for a maximum of 1 month after the impregnation date. Freezing minimizes the possibility of the sodium bicarbonate reacting with interfering substances present in the air.

8.7 Final Filter Acceptance Test

10 filters are selected randomly from the newly extracted filters. The filters are extracted with 15 mL of DI water and sonicated for 3 hours. The solutions are filtered and the extracts are analyzed. The hexavalent chromium values must be below 50 ppt. The filters are discarded if they are above the 50 ppt. If they are below 50 ppt, the filters are stored in a refrigerator (LAB 4) at approximately 4°C.

9.0 CHAIN OF CUSTODY

9.1 Pre-sampling

The site operators pick up the prepared filters that are mounted in black rings and placed in labeled plastic Petri dishes on work bench Q. Filter mounting and placement in Petri dishes are performed with great care to avoid contamination. Each Petri dish is labeled with a sample ID (Figure 1) and packaged in an individual Ziploc® bag with the chain of custody as generated through the Laboratory Information Management System (LIMS) attached to it. This chain of custody specifies the sampling ID, site, and date. The site operators have designated spaces to write all necessary information in regards to the sample on the chain of custody (Appendix A).

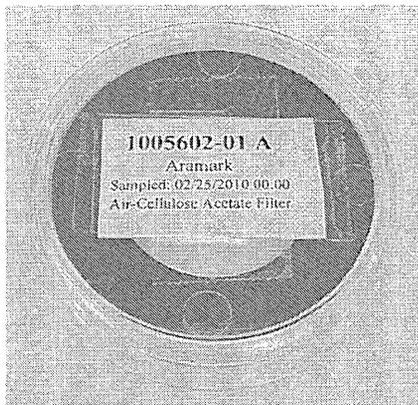


Figure 1. Labeled mounted impregnated 37 mm cellulose filter in a Petri dish

9.2 Post-sampling

Filters are received in the laboratory with the sample ID labeled on the plastic Petri dishes and accompanied by the corresponding chain of custody sheet(s). A printout obtained from the Xontech 920 sampler containing the retrieval date, air volume, average flow rate, and duration of sampling is submitted with the chain of custody. Any information relevant to sampling or the sample is written on the chain of custody sheet. The Senior Chemist receives the samples, inspects the filters for abnormalities, and reviews the chain of custody sheets for accuracy. If a problem is discovered, it is resolved with the station operator. If a filter is found to be invalid, the reason is entered on the chain of custody sheet and a qualifier is indicated for the sample in the LIMS system. The samples are stored in a refrigerator (LAB 1) at approximately 4°C until the samples are extracted. If a problem with the chain of custody is discovered later, it is returned to the Senior Chemist to resolve. The Senior Chemist contacts the station

operator for clarification, which could lead to corrections on the chain of custody and/or invalidation of the sample. A sample could be classified as invalid due the following reasons:

Filter contamination	Filters are either dropped or contaminated by any foreign matter (i.e. dirt, finger marks, ink, liquids)
Damaged or torn	Filters with tears or pinholes which occurred before or during sampling
Flow rate	Average flow rate is less than 9.0 LPM
Flow rate	Average flow rate is greater than 14.0 LPM
Flow rate	Start and stop flow rates differ by more than $\pm 10\%$
Flow rate	Average flow rate differs from the start or stop flow rates by more than $\pm 10\%$
Duration	Samplers starting before 2300 hours and after 0100 hours
Duration	Samplers operating less than 23 hours or more than 25 hours
Printout	Sample printout is not complete or missing and data cannot be retrieved
Power failure	Duration parameters are violated due to a power failure

10.0 FILTER EXTRACTION

10.1 Batching Samples for Extraction

The ambient filter samples are retrieved from the freezer with their corresponding chain of custody. The samples are then batched using the LIMS.

1. From the home screen select "Laboratory" → "Batch"
2. Click "Add"
 - a. select "Hexavalent Chromium for IC" in drop down menu located under "Preparation Method"
 - b. select "Particulates" in drop down menu located under "Batch Department"
 - c. select "Air" in drop down menu located under "Batch Matrix"
 - d. under "List Analyses by" make sure "Preparation" is selected and "Hexavalent Chromium for IC" is selected in drop down menu
 - e. under "Available" select "Hexavalent Chromium" and press "→" to transfer "Hexavalent Chromium" to "Included" (initial volume should reflect 1 mL and final volume 15 mL)
 - f. click "Save"
 - g. a batch number should automatically be generated
3. click "Bench Sheet"

- a. click "Edit"
 - b. click "Add"
 - c. select "Client Sample (By Container)"
 - d. "All Sample Containers Screen" will appear
 - e. select samples of interest by pressing the "Ctrl" key and left mouse clicking the samples
 - f. once the samples have been selected, right mouse click and select "Include Selection"
 - g. close the "All Sample Containers" screen
4. For QC samples (spikes, blanks, duplicates, etc), click "Add"
- a. select QC samples of interest
 - b. the QC samples will be listed separately from the other samples
 - BLK1 (Blank) = DI water and a cellulose filter NOT impregnated with NaHCO_3
 - BS1 (Lab Control Sample) = 150 μL of 20 ppb Cr^{+6} spike solution, DI water and a cellulose filter NOT impregnated with NaHCO_3
 - BLK2 (Blank) = DI water and a cellulose filter impregnated with NaHCO_3
 - BS2 (Lab Control Sample) = 150 μL of 20 ppb Cr^{+6} spike solution, DI water and a cellulose filter impregnated with NaHCO_3
 - c. if a spike sample is selected, additional information must be added
 - d. right mouse click the spike sample and select "Spike 1 ID"
 - e. "Particulate Spike Mixes" menu should appear
 - f. double click the desired spike solution (Hex Cr 20 ppb spike)
 - g. right mouse click the spike sample and select "Spike 1 Type"
 - h. "QC Sample Properties" should appear
 - i. in drop down menu select "Post-Prep" and press "Apply"
 - j. to add spike amount, right mouse click the spike sample and select "Spike 1 Amount"
 - k. enter the amount (150 μL) in "QC Sample Properties" and press "Apply"
 - l. Click "Save"
 - m. Click "Done"

10.2 Sample Extraction

Due to oxidation/reduction and the potential conversion of Cr^{+6} to Cr^{+3} , the extraction is performed immediately prior to analysis. Hexavalent chromium concentrations have been

shown to decrease significantly with time. It is important that the IC be equilibrated and ready for analysis.

The sample order is generated by the LIMS during the batching process. The samples are then recorded in a laboratory notebook. One Teflon® (30 mL) extraction vessel or polypropylene (50 mL) extraction vessel is used for each filter. Each extraction vessel is labeled with the filter number. Gloves are worn to prevent sample contamination. Using clean Teflon® tweezers, filters are removed from the black/blue ring holders and placed in the labeled extraction tubes. Water blanks, water spikes, filter blanks and filter spikes are prepared with each set of extractions. The maximum number of samples that can be batched are 35 filters. Add 15ml of deionized water to each sample and cap the tubes tightly with screw caps. Place the rack of Teflon® or polypropylene extraction vessels in a sonicator bath and sonicate for three hours. After three hours, remove the rack of Teflon® test tubes. Filter the samples using 20 mL disposable syringes and 0.22 µm PES filters.

Transfer approximately 8 ml of extracted samples to Dionex IC auto sampler vials (10 mL). Place the vials in the sampler tray and then onto the auto sampler. Extracts are refrigerated at approximately 4 °C until all analyses and data review is completed.

11.0 FILTER ANALYSIS

11.1 Analysis

A DI water blank followed by a 100 ppt and 500 ppt solution are analyzed before the IC is calibrated. The IC is calibrated using the 50 ppt, 100 ppt, 250 ppt, 500 ppt, and 1000 ppt calibration standards prepared as per Section 7.1. If needed, a 5000ppt standard can be added as well. The control standards (250ppt, 1000ppt) and the check standards (100ppt, 500ppt) are prepared according to Sections 7.2 and 7.3. They are analyzed after the instrument has been calibrated. Ambient air samples are analyzed in duplicate, followed by analysis of a DI water blank and check standards after every ten samples. In addition, the check standards and control standards are analyzed at the end of every sequence (sample sequence in Appendix B). When the Cr⁺⁶ concentration in a sample is above the calibration range (1000 ppt), dilutions are performed until the sample concentration falls into the calibration range. Serial dilutions are preferred to minimize error.

12.0 CALCULATIONS

$$\text{12.1 } \frac{\text{Nanograms}}{\text{Cubic Meter}} = \frac{(\text{Average of Duplicate Sample (ng/L)}) \times \text{Extraction Volume (L)}}{\text{Air volume (m}^3\text{)}}$$

13.0 QUALITY CONTROL

A quality control summary table is in section 18.0. A flow chart outlining the quality control process is in section 19.0.

13.1 Limit of Detection

The limit of detection (LOD) is a value that is based on statistical information. The LOD is described as the lowest concentration an analyst can quantify within a certain confidence level. The calculated limit of detection for the method is determined by analyzing a low standard (i.e. 50 ppt) ten times. The method's calculated limit of detection is determined as follows:

$$\text{LOD} = T(\text{SD})$$

Where $T_{0.99} = 3.29$, so $\text{LOD} = 3.29(\text{SD})$

SD = standard deviation of ten replicate analyses of a standard solution

The published LOD, which is the LOD that is used when reporting finalized data to the public, is 20 ppt. This LOD considers variation of instrument performance over time due to degradation of columns, lamps, and detectors. The published LOD is based on the calculated LOD and the chemist's experience with the method and instrument. The LOD is performed twice a year.

13.2 Linearity

Five and/or six standards are analyzed with each analytic sequence producing a linear regression calibration curve. This curve is examined for a correlation coefficient of 0.999 or better. If the correlation coefficient is less than 0.999, the standards are reanalyzed.

13.3 Control Limits

Controls are prepared from a second source of Cr^{+6} stock. They are analyzed after the calibration is complete and at the end of sample analysis. Control limits are historically derived from previously analyzed control samples. The limits are determined by

calculating the mean and standard deviation (STDEV) of historical data. The limits are defined as below:

$$\begin{aligned}\text{Upper Control Limit (UCL)} &= \text{mean} + 3\text{sd} \\ \text{Upper Warning Limit (UWL)} &= \text{mean} + 2\text{sd} \\ \text{Lower Warning Limit (LWL)} &= \text{mean} - 2\text{sd} \\ \text{Lower Control Limit (LCL)} &= \text{mean} - 3\text{sd}.\end{aligned}$$

Control charts and graphs are generated monthly. When one or both of the control values are out of the acceptable limits, then the instrument is evaluated for problems and appropriate corrective action is taken. Affected samples are re-analyzed until the control is within limits.

13.4 Method Detection Limit (MDL)

The MDL is determined annually. A standard is spiked onto at least seven prepared filters at a concentration three times the estimated detection limit. These filters are extracted according to the method outlined. The method detection limit should be less than 0.02 ng/mL which corresponds to an overall limit of detection of 0.02 ng/m³ for a 17 cubic meter ambient air sample.

13.5 Check Standards

Check standards (100 ppt and 500 ppt) are analyzed prior to and after the initial calibration, after every tenth sample, and at the end of all sample analyses. Check standard limits are $\pm 15\%$ of the target concentration. If one or more check standards are not within limits, affected samples are re-analyzed until all check standards are in control.

13.6 Initial Calibration Blank

DI water blank is analyzed before the initial check standards. Values must be below the MDL.

13.7 Filter Blanks

There are two types of blanks: a sodium bicarbonate impregnated cellulose filter blank and a non-impregnated cellulose filter blank. The blanks are analyzed with each set of extracted filters. Impregnated and non-impregnated filter blanks test for any contamination either in the deionized water used to extract the sample set or on the filter. Non-impregnated filter blanks should be below MDL. Impregnated filter blanks should be below 50 ppt.

13.8 Laboratory Control Samples

Spikes are performed using 200 ppt Cr⁺⁶ spiked onto a non-exposed filter. A spike is extracted and analyzed with each sample set. It is usually analyzed after the filter blank. The filter spike calculated concentration is 200 ppt. The spike recovery limit is ±20%. If the spike recovery exceeds ±20%, the solution is reanalyzed. If the spike recovery is still out of the allowable ±20%, the solution is re-prepared and reanalyzed. If the previous steps are insufficient, the samples are invalidated and further investigation is performed.

13.9 Duplicate Analysis

Every sample is analyzed in duplicate. If the values are not within 15%, the sample is reanalyzed.

14.0 LIMS - EXPORTING, ENTERING, AND REVIEWING DATA

14.1 Exporting data from Chromeleon® 6.8 to LIMS

1. Open the Chromeleon® 6.8 program
2. Select analysis date of interest on the left column by a single left mouse click (the right column will display samples analyzed on selected date)
3. Left mouse click the first sample of interest and select the rest of the samples by pressing down the shift key and down arrow key simultaneously until all samples have been selected
4. Go to “File” and select “Batch Report” from the drop down menu
 - a. unselect “Peak Analysis”
 - b. select “Integration, Calibration (Curr. Peak), Calibration (Batch)”
 - c. uncheck “Printout”
 - d. check “Export”
 - e. in the “Export Wizard: Common Options” check “ASCII text format (*.txt)”
 - f. click “Next”
 - g. select “Integration” from drop down menu
 - h. “None” should be selected in the Export Raw Data section
 - i. click “Finish”
 - j. click “OK”
 - k. once “Batch Report” export has reached 100% select “OK”
5. For archiving previously analyzed samples, follow instructions below

- a. right click on “Start”
- b. select “Explore”
- c. file location: Local Disc C → Documents and Settings → SOUTH COAST AIR QUAL → SOUTH COAST AIR QUAL’S Documents → Chromeleon → CR6_System → open file with date of interest
- d. change “Sample Name” to Sample ID ELEMENT assigns (i.e. 0930911-01)

14.2 Entering and Reviewing Data in Element

1. From the home screen select “Laboratory” → “Data Entry/Review”
2. select “Particulates”
3. select batch number of interest
4. select the “Data Entry” tab
 - a. click “Create”
 - b. click “Datatool” and select samples of interest and click “Done”
 - c. click “Merge Files”
 - d. click “Done”
 - e. click “Save”
5. select the “Data Review” tab
 - a. click “Query”
 - b. review final results
 - c. right click on data and select “View Details”
 - d. fields in red should be reviewed (fix or add qualifier as necessary)
 - e. make changes by selecting “Edit” in “Data Review” tab
6. Highlight all samples to change status
 - a. right click in sample area
 - b. select “Update Status” and click “Update to Analyzed”
7. Highlight all samples to lock samples
 - a. right click in sample area
 - b. select “Lock”

15.0 HAZARDOUS WASTE

15.1 Eluent Neutralization

The eluent waste is acidic. Neutralize the waste by dissolving sodium hydroxide into the solution. The waste, originally clear, will change to a pink hue when it is close to being

neutral in pH. Use pH strips to confirm the pH level. The solution should be neutral before placing into a labeled waste disposal drum. For the location of the hazardous waste drum and more information concerning the removal of hazardous waste contact the hazardous waste coordinator or Chemical Hygiene Officer.

15.2 Hexavalent Chromium Waste

In the laboratory, there are hazardous waste containers for hexavalent chromium working standards. Keep the stock standards in their individual containers. Do not place the stock standards in the working standards hazardous waste container. Contact the Hazardous Waste Coordinator or Chemical Hygiene Officer for the removal of hexavalent chromium stock and working standards.

16.0 MAINTENANCE

The ICS-3000 is serviced annually by Dionex®. Please refer to the ICS-3000 Ion Chromatography Manual on the Dionex® website for routine maintenance and troubleshooting.

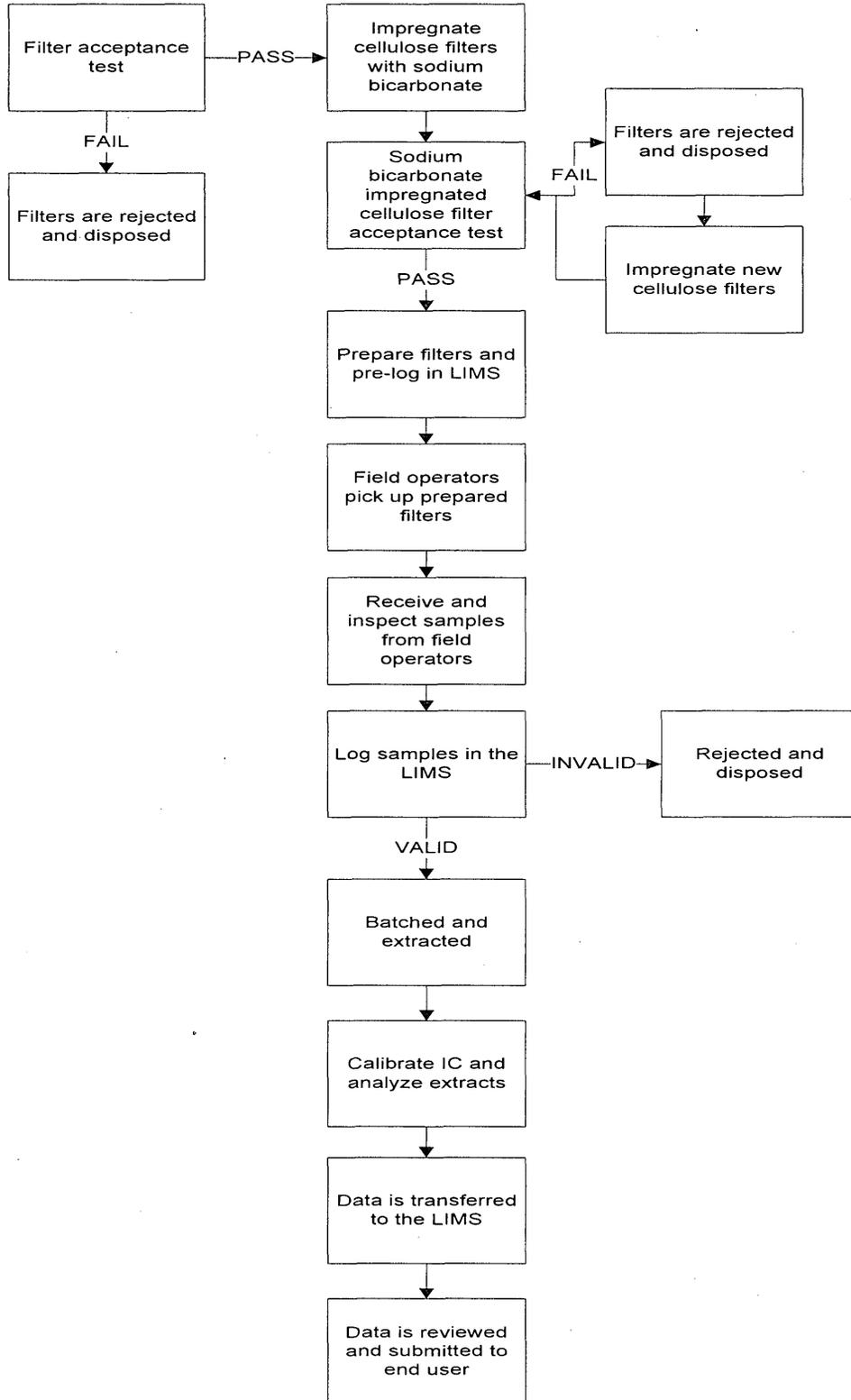
17.0 REFERENCES

1. California Air Resources Board Method SOP MLD-039: "Standard Operating Procedure for the Analysis of Hexavalent Chromium in Ambient Air by Ion Chromatography"
2. Dionex Technical Note TN24: Determination of Chromium by Ion Chromatography, Dionex Corporation, July 1991.
3. U.S. Environmental Protection Agency Method SOP 5-03: "Standard Operating Procedure for the Determination of Hexavalent Chromium In Ambient Air analyzed By Ion Chromatography (IC)"
4. SOP00052 Standard Operating Procedure for Xontech® 920.
5. SOP 00102 Standard Operating Procedure for Visual Inspection & Acceptance of Cellulose Fiber Filters.

18.0 QUALITY CONTROL SUMMARY TABLE

Parameter	Frequency	Acceptance Criteria	Corrective Action
Performance Qualification	Annually	LOD - ≤ 20 ppt Linearity - correlation coefficients ≥ 0.999 Blank Test ≤ 20 ppt	1) Check instrument function 2) Perform repair 3) Requalify instrument 4) Submit documentation to QA Branch
Initial Calibration Blank	One per batch, before the initial check standards	Below MDL	1) Reanalyze 2) Prepare blank again and re-analyze. 3) Correct contamination and reanalyze blank. 4) Flag data of all samples since the last acceptable blank.
Initial 5/6 point calibration standards	Before every sequence	Correlation coefficient 0.999	1) Repeat analysis of calibration standards. 2) Reprepare calibration standards and reanalyze.
Initial Check Standards	Before every sequence, prior to and after the initial calibration	Recovery 85-115%	1) Repeat analysis of initial check standards. 2) Repeat analysis of calibration standards. 3) Reprepare calibration standards and reanalyze.
Control Standards	Following the initial calibration and at the end of the analytical sequence	Recovery 85-115%	1) Reanalyze. 2) Reprepare control standards and reanalyze. 3) Reprepare calibration standards and reanalyze.
Check Standards	Every 10 samples and at the end of the analytical sequence	Recovery 85-115%	1) Repeat analysis of check standards. 2) Reprepare check standards 3) Flag data bracketed by unacceptable check standards.
Filter Blanks	Two for an extraction set	Non-impregnated filter (below MDL) Impregnated filter (< 50 ppt)	1) Reanalyze 2) Flag data of all samples since the last acceptable blank.
Laboratory Control Sample	Two for an extraction set	Recovery 80-120%	1) Reanalyze. 2) Reprepare spike and reanalyze. 3) Flag data of all samples since the last acceptable spike.
Replicate Analysis	Duplicate and/or Replicate samples only	RPD $< 15\%$ for concentrations greater than 5x the MDL	1) Check integration. 2) Check instrument function. 3) Flag samples.
Collocated samples	Once every ten samples	$\pm 30\%$ for values > 5 x MDL	1) Investigate and discuss with Ambient Monitoring and Quality Assurance Branch

19.0 FLOWCHART FOR HEXAVALENT CHROMIUM ANALYSIS



APPENDIX A
CHAIN OF CUSTODY



Riverside Deposition Project
South Coast Air Quality Management District
Special Monitoring Field Sample Log

Cr(VI)

Location: **Aramark**
Sample Begin Date: **12/28/2009 00:00**
Sample End Date: _____
Retrieval Date: _____
Filter Load Date: _____

Lab No: **0936201-01**
Date Sample Received: _____
Reference No: _____
Analyst: _____

Sample Elapsed Time	Recorded By	Average Flow Rate	Air Volume
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Comments:

Chain of Custody:

Relinquished By	Received By	Section/Group	Date/Time
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Relinquished By	Received By	Section/Group	Date/Time
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APPENDIX B
SAMPLE SEQUENCE

Sample #	Sample Name	Location	Comments
1	REAGENT BLANK	7	
2	100 TEST	1	
3	500 TEST	3	
4	STD2	14	50 PPT
5	STD3	9	100 PPT
6	STD4	10	250 PPT
7	STD5	11	500 PPT
8	STD6	12	1000 PPT
9	STD7	13	5000 PPT
10	CONTROL 250 PPT	5	
11	CONTROL 1000 PPT	6	
12	100 CHECK	1	
13	500 CHECK	4	
14	BLANK	7	
15	B002002-BLK1	15	Blank 2/4/10
16	B002002-BLK1	15	Blank 2/4/10
17	B002002-BS1	16	Blank Spike 2/4/10
18	B002002-BS1	16	Blank Spike 2/4/10
19	B002002-BLK2	17	Imp Blank 2/4/10
20	B002002-BLK2	17	Imp Blank 2/4/10
21	B002002-BS2	18	Imp Blank Spike 2/4/10
22	B002002-BS2	18	Imp Blank Spike 2/4/10
23	1002901-01	19	Aramark 1/29/10
24	1002901-01	19	Aramark 1/29/10
25	100 CHECK	1	
26	500 CHECK	3	
27	1003202-01	20	Aramark 2/1/10
28	1003202-01	20	Aramark 2/1/10
29	1002901-02	21	Colton HS 1/29/10
30	1002901-02	21	Colton HS 1/29/10
31	1003202-02	22	Colton 2/1/10
32	1003202-02	22	Colton 2/1/10
33	1002901-03	23	Plumber's Union 1/29/10
34	1002901-03	23	Plumber's Union 1/29/10
35	1003202-03	24	Plumber's Union 2/1/10
36	1003202-03	24	Plumber's Union 2/1/10
37	100 CHECK	2	
38	500 CHECK	4	
39	CONTROL 250 PPT	5	
40	CONTROL 1000 PPT	6	
41	BLANK	7	
42	BLANK	7	