

California Environmental Protection Agency



SOP MLD039

**STANDARD OPERATING PROCEDURE FOR THE
ANALYSIS OF HEXAVALENT CHROMIUM AT
AMBIENT ATMOSPHERIC LEVELS BY
ION CHROMATOGRAPHY**

Northern Laboratory Branch
Monitoring and Laboratory Division

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1 Introduction

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 associated with respiratory cancer. Exposure is primarily associated with the chrome plating and anodizing process, and emissions from chromate treated cooling towers.

Hexavalent chromium has been measured in ambient air at sites located throughout California. Cellulose filters are exposed to ambient air using a Xontech 920 toxic air sampler. Samples are taken every twelve days, year round. To achieve lower detection limits, in certain cases the exposed filters may be composited from the same site and analyzed as a group. The analysis procedure for hexavalent chromium from exposed 37mm cellulose filters is described in this document.

2 Summary of Method

Method MLD039 determines Cr^{+6} from bicarbonate impregnated ashless cellulose filters exposed to ambient air, which are submitted to the laboratory by site operators. The filters are extracted in deionized water via sonication for three hours. 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 pH of the eluent. After separation through the column, hexavalent chromium forms a complex with the diphenylcarbohydrazide (DPC) which is detected at 520 nm. The peak analysis is determined using Dionex Peaknet chromatography software, version 5.1.

3 Interferences and Limitations

- 3.1 Sodium carbonate used as the stabilizing media in Cr^{+6} filters was observed to cause interferences with the analysis.

- 3.2 Higher concentrations of the sodium bicarbonate impregnating solution may cause flow restrictions during ambient air sampling. The use of smaller pore size impregnated filter has shown to cause definite restrictions during sampling.

4 Instrument and Equipment

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

- 4.1 The Dionex Ion Chromatographic System is comprised of modular units purchased from the Dionex Corporation:

1. Dionex gradient pump;
2. Reagent delivery module;
3. Variable wavelength detector;
4. Automated sampler, which is controlled directly from the PeakNet workstation.

- 4.2 IC Operating conditions:

Sample loop volume	400 μ L
Analytical column	Dionex, Ion Pac CS5
Guard column	Dionex, Ion Pac CG5
Eluent solution	2mM Pyridinedicarboxylic acid (PDCA) 2mM Disodium hydrogen phosphate heptahydrate 10mM Sodium iodide 50mM Ammonium acetate 2.8mM Lithium hydroxide monohydrate
Eluent flow rate	1.0 mL/min
Post-column reagent	2mM Diphenylcarbohydrazide (DPC) 10% Methanol 0.9N Sulfuric acid
Post-column flow rate	0.5 mL/min
Mixing device	Reaction coil
Detector wavelength	520nm
Acquisition Software	Dionex Peaknet, version 5.1

5 Materials and Chemicals

- 5.1 Materials:

1. 37mm diameter cellulose filters
2. Black filter ring holders
3. Plastic petri dishes, large enough to hold a 37mm filter

4. Circular labels specifying the Cr⁺⁶ program
5. Volumetric flasks: 1L and 2L sizes
6. Wide-mouth polyethylene storage bottles: 500mL and 1L sizes
7. Analytical balance
8. Pipettor with disposable pipet tips: 100µL and 2.5 mL pipettors
9. Teflon centrifuge tubes with caps
10. Ultrasonicator
11. Hot plate/stir plate
12. Large glass petri dish
13. High purity helium
14. Repipettor 25 mL

5.2 Chemicals: All chemicals are at least spectrophotometric grade.

1. Pyridine 2,6-Dicarboxylic Acid (PDCA)
2. Disodium hydrogen phosphate heptahydrate (Na₂HPO₄-7H₂O)
3. Sodium Iodide (NaI)
4. Ammonium Acetate (CH₃CO₂NH₄)
5. Lithium hydroxide monohydrate (LiOH)
6. 1,5-diphenylcarbohydrazide (DPC)
7. Methanol (CH₃OH)
8. Sulfuric acid (H₂SO₄)
9. Sodium bicarbonate (NaHCO₃)
10. Nanopure ASTM Type 1 deionized water (>16 MΩ-cm)

5.3 Hexavalent chromium stocks are National Institute of Science and Technology (NIST) certified. Two stocks solutions are purchased, one for making working standards, the other for making a working control. The two solutions are of different sources, whether they are from different lot numbers or different companies.

6 Preparation of Eluent

6.1 Stock eluent is prepared in nanopure water. The following list describes the concentrations of each chemical when making a 1liter solution of eluent stock:

Chemicals	Concentrations
PDCA	20mM (3.34g/L)
Disodium hydrogen phosphate heptahydrate	20mM (5.36g/L)
Sodium Iodide	100mM (15.0g/L)
Ammonium Acetate	500mM (38.5g/L)
Lithium hydroxide monohydrate	28.0mM (1.10g/L)

Heat approximately 700mL nanopure deionized water in a 1L volumetric flask on a hot plate/stir plate. Do not boil water. Add the PDCA and let dissolve before adding the remaining chemicals. The PDCA is slow to dissolve. When the PDCA has dissolved add the remaining chemicals to the flask. Once all chemicals have

dissolved, turn off the heat and let the flask cool. Bring to volume with nanopure and transfer eluent stock to a 1L wide-mouth polyethylene storage bottle.

- 6.2 The working eluent is prepared by diluting 100mL of the eluent stock to volume in a 1L volumetric flask. Transfer the eluent to the eluent reservoir on the IC. The pH of the diluted eluent is between 6.70 and 6.80.

7 Preparation of Post-Column Reagent

Dissolve 0.5g of DPC in 100mL of HPLC grade methanol in a 1L volumetric flask. When all DPC has dissolved, add about 500mL of nanopure water, then 25mL of 96% spectrophotometric grade sulfuric acid. Bring to volume with nanopure water. Transfer the post-column reagent to a wide-mouth 1L bottle that will then be placed in the post-column reagent delivery module on the IC.

8 Preparation of Hexavalent Chromium Standards and Controls

Both hexavalent chromium calibration and control stocks are NIST traceable. Hexavalent chromium stocks are usually in 1000 μ g/mL concentrations. All standards are stored in the refrigerator until ready for use. The solutions are brought to room temperature prior to analysis.

- 8.1 Both the calibration and control standards are prepared from a 100ng/mL Cr⁺⁶ solution. It takes two dilutions to make a 100ng/mL sub-stock. First dilute 0.5mL of 1000 μ g/mL Cr⁺⁶ stock into a 50mL volumetric flask. This makes a 10 μ g/mL Cr⁺⁶ solution. Place 0.5mL of the 10 μ g/mL Cr⁺⁶ sub-stock in a 50mL volumetric flask. Bring to volume. This second sub-stock solution concentration is 100ng/mL hexavalent chromium.
- 8.2 Calibration Standards: Dilute appropriately to make a sub-stock with a concentration of 100ng/mL. The working standards are prepared in 100mL volumetric flasks:

Concentration (ng/mL)	Aliquot (mL) of 100ng/mL
0.5	0.5
1.0	1.0
1.5	1.5
2.0	2.0

- 8.3 Control Standards: The control is prepared from a secondary source stock. The control concentration is 1.0ng/mL. Prepare a sub-stock with a concentration of 100ng/mL. Place 1.0mL of the 100ng/mL sub-stock in a 100mL volumetric flask. Bring to volume.

9 Preparation of Sodium Bicarbonate Impregnating Solution

Filters are soaked in a 0.12mM sodium bicarbonate solution. Dissolve 5.0 g of sodium bicarbonate in nanopure water in a 500mL volumetric flask. Bring to volume and transfer the solution to a wide-mouth polyethylene storage bottle.

10 Preparation of Hexavalent Chromium Filters

Whatman #41 37 mm cellulose filters are handled with either clean Teflon-coated or plastic tweezers or with disposable PVC gloves. Pour part of the sodium bicarbonate impregnating solution in a large clean glass petri dish. After inspecting the filters for any tears, holes, or contamination, place the cellulose filters in the solution. Make sure all filters are soaking in the impregnating solution. After soaking the filters a few minutes, remove the filters from the solution and place them on a plastic net or drying rack.

Place the dried filters in a Ziploc bag. On the outside of the bag place the following information: lot number of the filters, date of filter preparation, and initials of the preparer. Place in the freezer until filters are needed. The freezing reduces the sodium bicarbonate from reacting with possible interfering substances present in the air.

- 10.1 Filter Mail-Out Preparation: The filters are sent to the site operators in black rings that are placed in plastic petri dishes. First place a circular label on each petri dish. This label contains spaces where the site operator will write down the site and sampling date. Place the female portion of the black ring on a clean surface or clean towel. Place a prepared filter onto the ring. Snap the male portion of the ring on top. Place the filter into the plastic petri dishes. Packs with nine filters are then shipped out. Mail-outs occur about two weeks before the end of the quarter. Place these filters in a cool, dry place.

11 Filter Log-In

Filters are received in the laboratory with site name and sampling date written on the plastic petri dishes. A strip of paper with data (i.e. date received, average flowrate, duration, and volume) from the Xontech 920 sampler is taped to the outside of this petri dish. This data is logged into the Laboratory Information Management System (LIMS) (i.e. SQL*LIMS). All filters are assigned a barcode identification number. Remove the black ring holders, and place the filter in the petri dish. Place all samples in the freezer until ready for analysis.

- 11.1 The following is a list of invalid 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
Flowrate	Average flowrate is less than 9.0LPM
Flowrate	Average flowrate is greater than 14.0LPM

Flowrate	Start and stop flowrates differ by more than $\pm 10\%$
Flowrate	Average flowrate differs from the start or stop flowrates 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
Power failure	Duration parameters are violated due to a power failure
Printout	Sample printout is not complete or missing and data cannot be retrieved

12 Filter Analysis

Due to oxidation/reduction and the conversion of Cr^{+3} and Cr^{+6} , the extraction is performed immediately prior to analysis. Hexavalent chromium concentrations have been shown to increase significantly with time. It is important that the IC be equilibrated and ready for analysis.

Calibrate the IC using four standards prior to analyzing samples.

After the calibration is performed a control, check standard, water blank, filter blank, and filter spike are determined. The ambient air samples are analyzed along with a check standard after every tenth sample. At the end of the sample run a check standard and a control are again determined.

- 12.1 First, printout a hexavalent chromium worklist to confirm which samples need to be extracted and analyzed. Prepare the water and filter blanks, filter spikes, and ambient air samples by placing the proper filter into an assigned 50mL Teflon test tube using disposable PVC gloves. Add 15mL of nanopure water and cap the test tube tightly. Place the rack of test tubes in a sonicator bath for three hours. After three hours, remove the rack of test tubes.
- 12.2 Transfer approximately 5mL of extracted sample to a corresponding Dionex IC autosampler vial, which is in an autosampler cartridge. For replicate samples, pour approximately 2.5 mL of the extracted sample into a vial. This conserves Cr^{+6} samples. Place the cartridge on the autosampler to be analyzed. Extracts are refrigerated until all analyses are completed.

13 Quality Control

- 13.1 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 with a certain confidence level. The calculated limit of detection for the method is determined by analyzing a low standard (i.e. 0.25 ng/ml) seven times. The method's calculated limit of detection is determined according to 40 CFR, Appendix B, as follows:

$$\text{LOD} = T_{(n-1, 1-\alpha=0.99)} (\text{sd})$$

where,

$T_{n-1, \alpha=0.99} = 3.143$ for seven replicates

sd = standard deviation of seven replicate analyses of a standard solution

The published LOD, which is the LOD that is used when reporting finalized data to the public, is 0.2 ng/mL. 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 of the method and instrument.

- 13.2 Four known standards are analyzed for the linear regression calibration curve. Check the linear curve and correlation coefficient. If the correlation coefficient is less than 0.950, the standards are re-analyzed.
- 13.3 Controls are prepared from a second source of Cr⁺⁶ stock. They are analyzed after the calibration is complete and at the end of the sample run. Control limits are historically derived from previously analyzed control samples. The limits are determined by calculating the mean and standard deviation (sd) of historical data. The limits are defined as below:

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

If 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 Check standards are the 1.0 ng/mL calibration standard analyzed every tenth sample. Check standard limits are $\pm 20\%$ 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.
- 13.5 There are two types of blanks: a filter blank and a water blank. Blanks are analyzed with each set of extracted filters. Water and filter blanks are analyzed in the beginning of a sample run. Water and filter blanks test for any contamination either in the nanopure water used to extract the sample set or on the filter.
- 13.6 Spikes are unexposed filters spiked with 15 μ L of the 1.0 μ g/mL Cr⁺⁶ solution. Place the dried filters in a storage bag with the appropriate identification, such as date filters were spike and the chemist's initials. Place the bag in the freezer until ready to use. A spike is extracted and analyzed with each sample set. It is usually analyzed after the filter blank. The filter spike calculated concentration is 1.0ng/mL. The spike recovery limit is $\pm 20\%$.

14 Hazardous Waste

- 14.1 The eluant waste is acidic. Neutralize the waste by dissolving sodium hydroxide to 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 waste removed from the satellite area should be neutral before placing into the appropriately labeled drum. For location of the hazardous waste drum and more information concerning the removal of hazardous waste contact the hazardous waste coordinator.

- 14.2 In the laboratory there should be a satellite hazardous waste container for the 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 for the removal of hexavalent chromium stock and working standards.

15 References

1. California Air Resources Board Method 105: Procedure for the Analysis of Hexavalent Chromium at Ambient Atmospheric Levels by Ion Chromatography.
2. Dionex Technical Note TN24: Determination of Chromium by Ion Chromatography, Dionex Corporation, July 1991.