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Standard Operating Procedure for the Determination of Hexavalent Chromium In Ambient Air Analyzed By Ion Chromatography (IC)

Work Assignment 5-03

Prepared for:
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DISCLAIMER

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1.0 IDENTIFICATION AND PURPOSE

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 generated anthropogenically from a number of commercial and industrial sources. Hexavalent Chromium (Cr^{6+}) 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 and it is primarily associated with the chrome plating and anodizing process and emissions from chromate-treated cooling towers. This standard operating procedure (SOP) provides the analytical procedures for the analysis of Cr^{6+} by ion chromatograph (IC).

2.0 MATRIX OR MATRICES

Hexavalent chromium has been measured in the air across the county. A procedure for sample preparation was written by California Air Resources Board (CARB-039) and has been modified in the procedure listed below. Sodium Bicarbonate impregnated cellulose filters are exposed to ambient air using hexavalent chromium samplers.

3.0 METHOD DETECTION LIMIT

The method detection limit (MDL) is determined every year according to the procedure in 40 CFR, Part 136, Appendix B. 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 below. The method detection limits should be less than 0.19 ng/mL.

4.0 SCOPE AND APPLICATION

This procedure provides step-by-step instructions for analyzing Cr^{6+} collected on Sodium Bicarbonate impregnated ashless cellulose filters exposed to ambient air.

5.0 METHOD SUMMARY

This SOP covers the determination of Cr^{6+} from bicarbonate-impregnated ashless cellulose filters exposed to ambient air and submitted to the laboratory. The filters are extracted in 20 mM Sodium Bicarbonate in deionized (DI) water via sonication for 1 hour. The extract is analyzed by ion chromatography using a system comprised of a guard column, an 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, the Cr^{6+} forms a complex with the 1,5-diphenylcarbohydrazide (DPC) which can be detected at 530 nm. See Section 21 for a summary of the method steps and Figure 24.1 for a method flow diagram.

6.0 DEFINITIONS

SOP	Standard Operating Procedure
IC	Ion chromatograph
MDL	method detection limit
DI	Deionized
UV/VIS	Ultraviolet-Visible
DPC	1,5-Diphenylcarbohydrazide
PCR	Post-column Derivatizing Reagent
APG	Advanced Gradient Pump
LCS	Laboratory Control Samples
MQO	Method Quality Objectives
ICV	Initial Calibration Verification
CCV	Continuing Calibration Verification
ICB	Initial Calibration Blank
CCB	Continuing Calibration Blank
PE	Performance Evaluation
g	gram
ng/mL	nanogram(s) per milliliter
L	liter(s)
mL	milliliter(s)
µL	microliter(s)
LPM	liter(s) per minute
M	molar
mM	millimolar
cm	centimeter(s)
nm	nanometer(s)
µm	micron(s)

7.0 INTERFERENCES

Sodium Carbonate used as the stabilizing medium on the Cr⁶⁺ on filters was observed to cause interferences with the analysis. Higher concentrations of the Sodium Bicarbonate impregnating solution may cause flow restrictions during the ambient air sampling. The use of an impregnated filter of smaller pore size has been shown to cause flow restrictions during sampling.

8.0 SAFETY

8.1 The IC does not require venting for toxic vapors, and elaborate safety precautions are unnecessary. Safety glasses must always be worn in the laboratory. Gloves are required during the handling of all hazardous solutions.

8.2 The compressed gas cylinders must be stored and handled according to relevant safety codes outlined in the corporate health and safety manual. The cylinders must

be secured to an immovable structure. They must be moved using a gas cylinder cart.

- 8.3 Calibration standards are purchase in dilute solutions from certified vendors. Standard laboratory practices for hazardous material handling should be employed for handling acids, derivatizing reagents and neat Cr⁶⁺ salts when these are used for analysis.

9.0 EQUIPMENT

The following equipment and materials are required for performing successful analysis of hexavalent chromium.

- 9.1 Automated IC and autosampler. This instrument is an analytical system complete with a chromatography compartment, a 1.0 mL autosampler syringe, an advanced gradient pump (AGP) with vacuum degas option, an eluent container set with rack, an eluent degas module, a Rheodyne injection valve, an UV/VIS absorbance detector, and a post-column pneumatic delivery package.
- 9.2 Data acquisition and processing software. The instrument is controlled and data is collected and processed using the software.
- 9.3 Instrument accessories. A waste container and a Helium regulator is needed to regulate the pressure source for the carrier gas and degassing of the eluents.

10.0 MATERIALS

This SOP assumes familiarity with the installation and operation of the instrument chromatography software system. For a more detailed instruction in the operations of the IC, please refer to that specific SOP and the instruments operations manual.

- 10.1 Materials required for analysis include 5 or 10 mL disposable syringes, a waste container, and a helium regulator that regulates the pressure source for the carrier gas and degassing of the eluents. Also, the specific guard, separator, and suppressor columns are listed below in Section 14.2.
- 10.2 Guard Column: Dionex IonPac NG1, or equivalent.
- 10.3 Analytical Column: Dionex IonPac AS7, or equivalent.
- 10.4 Nanopure ASTM Type I DI water: The water (> 16 MΩ-cm) should be used for preparing eluent, post-column derivatizing reagent, Sodium Bicarbonate solutions, and standards.
- 10.5 Volumetric flasks: 100 mL, 1 L, and 2 L.

- 10.6 Wide-mouth high-density polyethylene storage bottles: 125 mL.
- 10.7 Analytical balance.
- 10.8 Digestion vessels: Polystyrene tubes with caps and tube rack, 14 mL.
- 10.9 Ultrasonicator.
- 10.10 Glove box: The glove box should be supplied with a screen rack and ultra-pure nitrogen to purge while handling and drying filters.
- 10.11 Graduated cylinders: 50 mL, 100 mL, and 500 mL.
- 10.12 Large plastic containers for rinsing filters and filter baths. Three baths are needed.
- 10.13 Freezer: The freezer needs to measure less than -15°C .
- 10.14 Tweezers: Teflon® coated or plastic tweezers for handling filters.
- 10.15 Pipettes: 100 μL , 5000 μL , and 10 mL.
- 10.16 Disposable Nitrile gloves.

11.0 CHEMICALS, REAGENTS, AND STANDARDS

11.1 Eluent Stock

A standard eluent solution of the following reagents is prepared in DI water:

- C 250 mM Ammonium sulfate
- C 100 mM Ammonium hydroxide

In a 2 L volumetric flask, dissolve 33 g of Ammonium Sulfate in ~1 L DI water and add 7 mL of Ammonium Hydroxide. Dilute to 2 L with DI water.

11.2 Post-column Derivatizing Reagent (PCR)

In a 1 L volumetric flask, dissolve 0.5 g of 1,5-Diphenylcarbazide in 100 mL of HPLC-grade Methanol. While stirring, add 500 mL of DI water containing 28 mL of 98% sulfuric acid. This reagent is stable for four or five days. To minimize waste, it should be prepared in 1 L quantities as needed.

11.3 0.12 M Sodium Bicarbonate Impregnating Solution

In a 500 mL volumetric flask, dissolve 5.0 g of Sodium Bicarbonate in ~ 250 mL DI water. Dilute to 500mL with DI water.

11.4 20 mM Sodium Bicarbonate Solution

In a 1 L volumetric flask, dissolve 1.68 g of Sodium Bicarbonate in ~500 mL DI water. Dilute to 1 L with DI water.

11.5 Primary Stock Solutions

A primary stock solution 1000 µg/mL Cr⁶⁺ is available commercially or can be prepared by diluting 0.283 g of Potassium Dichromate (K₂CrO₇), dried at 100°C for one hour and diluted to 100 mL using DI water. Two primary stock solutions should be prepared and/or obtained from separate sources. One is to be used exclusively for the calibration standards and matrix spikes and the other for laboratory control standards (LCS).

11.6 Working Stock Solutions

The working stock solutions are 1000 ng/mL Cr⁶⁺. Working stock solutions should be prepared for both calibration standards and laboratory control standards/calibration verification. It is important not to use the same primary stock solution for both working stock solutions.

11.6.1 Calibration Working Stock Solution: Dilute 100 µL of the calibration primary stock solution to 100 mL using the 20 mM Sodium Bicarbonate in DI water solution.

11.6.2 Laboratory Control Working Stock Solution: Dilute 100 µL of the laboratory control primary stock solution to 100 mL using the 20 mM Sodium Bicarbonate in DI water solution.

11.7 Calibration Standards

The five calibration standards are prepared by diluting the calibration working stock solution to the concentrations specified below.

11.7.1 0.1 ng/mL Cr⁶⁺ - Dilute 10 µL of the working stock solution to 100 mL using the 20 mM Sodium Bicarbonate in DI water solution.

11.7.2 0.2 ng/mL Cr⁶⁺ - Dilute 20 µL of the working stock solution to 100 mL using the 20 mM Sodium Bicarbonate in DI water solution.

11.7.3 0.5 ng/mL Cr⁶⁺ - Dilute 50 µL of the working stock solution to 100 mL using the 20 mM Sodium Bicarbonate in DI water solution.

11.7.4 1.0 ng/mL Cr⁶⁺ - Dilute 100 µL of the working stock solution to 100 mL using the 20 mM Sodium Bicarbonate in DI water solution.

11.7.5 2.0 ng/mL Cr6+ - Dilute 200 µL of the working stock solution to 100 mL using the 20 mM Sodium Bicarbonate in DI water solution.

11.8 Calibration Verification Solution

As part of the quality assurance program in the evaluation of the data, a calibration verification from a secondary source at an intermediate concentration (0.5 ng/mL) is run as a check of the precision of the instrument and calibration. An Initial Calibration Verification (ICV) is run immediately following the calibration standards and Continuing Calibration Verifications (CCV) is run after every 10 samples.

11.8.1 Calibration Verification Solution Preparation - Dilute 50 µL of the LCS Spike Solution to 100 mL using the 20 mM Sodium Bicarbonate in DI water solution.

12.0 COLLECTION, PRESERVATION, SHIPMENT, AND STORAGE

12.1 Handling of filters

Whenever the filter is handled, clean Teflon⁷ coated or plastic tweezers are used with disposable Nitrile gloves. All filter preparation and extraction is completed in the laboratory Nitrogen purged glove box.

12.2 Preparation of filters

12.2.1 Soak filters in 10% nitric acid bath for a minimum of 2 hours and a maximum of 18 hours.

12.2.2 Rinse filters thoroughly with DI water. Check pH of the filters by placing a pH strip on top of the wet filter. The pH should match the DI water. Discard the tested filter.

12.2.3 Dry the filters completely on a screen rack in a Nitrogen purged glove box (approximately 3 hours). Filter appearance will become stiff after they have dried.

12.2.4 Soak the dried filters in the 0.12 M Sodium Bicarbonate impregnating solution overnight. If the filters are not completely dry before placing them in the impregnating solution, the solution will become dilute and will not collect samples as efficiently.

12.2.5 Dry the filters completely on a screen rack in a Nitrogen purged glove box.

12.2.6 Place dried filters into Petri dishes. Place these into a plastic freezer bag labeled with the batch number and store in a freezer until needed.

12.3 Preservation and Storage of filters

The filters are kept in the freezer until needed in the field for samples or used in the laboratory to prepare spikes or blanks during analysis. The filters are frozen to prevent the sodium bicarbonate from reacting with possible interfering substances present in the air.

12.4 Shipment of the filters

When preparing the filters for shipment, the filters are placed in the filter holder cartridge in the Nitrogen purged glove box to avoid sample contamination that might occur in the field. The filters are placed in a cooler packed with blue ice to keep the filters frozen. The filters/dishes, funnels, and chain of custodies are sent to the field approximately 1-2 weeks in advance. These filters are kept in freezers in the field.

13.0 CALIBRATION AND STANDARDIZATION

- 13.1 Prepare calibration standards at a minimum of five levels as described in Section 11.7. The initial calibration ranges from 0.1 to 2.0 ng/mL Cr⁶⁺. An acceptable correlation coefficient is ≥ 0.995 .
- 13.2 Analyze each calibration standard and tabulate the area response against mass injected. Follow the analytical procedures described in Sections 14.2. Use the results to prepare a calibration curve.
- 13.3 Use a Least Squares Linear Regression Calculation (Chromatographic software) to calculate a correlation coefficient, slope, and intercept. A correlation coefficient of at least 0.995 is required. See equation in Section 15.4. For each compound of interest, a regression line may be written:

$$y = mx + b$$

where:

y = dependent variable (response)

m= slope of regression line

b = intercept

x = independent variable (concentration)

- 13.4 The ICV is used to verify the internal calibration. Analyze an ICV after the initial calibration and analyze a CCV after every 10 samples, and at the end of the analysis batch. The primary stock solution for the ICV and CCV must be from a different source than what is used for the calibration standards. The recovery criteria are 85-115%. If the ICV or CCV is not within $\pm 15\%$ of target, prepare a new check standard and/or recalibrate the instrument.

14.0 PROCEDURE

14.1 Filter Extraction

Due to the oxidation/reduction and conversion problems of Cr^{3+} and Cr^{6+} , the extraction should be performed immediately prior to analysis. It is important that the ion chromatograph be equilibrated, calibrated and ready for analysis. One prepared, unused filter will be used for extraction blanks with every batch. Unused filters will also be used for blank spikes.

14.1.1 Remove the exposed filter from the Petri dish, inside the Nitrogen-purged glove box, using tweezers and disposable Nitrile gloves. Fold the filter, place it in a 14 mL polystyrene test tube and add 10 mL of the 20 mM Sodium Bicarbonate in DI water solution. Cap the tube tightly.

14.1.2 Place the tubes in a test tube rack and remove from the glove box. Place the tube rack in the sonicator for 1 hour.

14.1.3 After 1 hour of sonication, remove the tubes and put 5 mL of the sample extract into a 5 mL disposable autosampler vial. If replicate analyses are required, prepare another autosampler vial, otherwise, store the remaining extract in a refrigerator until all analysis of samples are complete.

14.2 Sample analysis

The analysis time is approximately 9 minutes. The following conditions are used for analysis.

14.2.1 Guard Column B Dionex IonPac NG1, or equivalent.

14.2.2 Analytical Column B Dionex IonPac AS7, or equivalent.

14.2.3 Eluent flow rate B 1.5 mL/minute (250 mM Ammonium sulfate and 100 mM Ammonium hydroxide).

14.2.4 Postcolumn Reagent flow rate B 0.5 mL/min (2 mM DPC in 10% Methanol and 1 N Sulfuric acid).

14.2.5 Detection Wavelength B 530 nm.

14.2.6 Sample Volume B 830 μL .

15.0 CALCULATIONS

The chromatographic software calculates sample concentrations based on the calibration values entered into the program. A peer reviewer should verify these values after analysis, and corrections can be made before reporting.

15.1 Method Detection Limit (MDL)

The MDL is determined every year according to the procedure in 40 CFR, Part 136, Appendix B. 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 limits should be less than 0.19 ng/mL.

An example calculation for the method detection limit, outlined in 40 CFR, Part 136, Appendix B, is shown below:

Example: Standard Deviation of 7 runs of 0.1 ng/mL = 0.007 x Student's t value at the 99% confidence level, which is 3.143.

$$\text{MDL} = 0.007 \text{ ng/mL} \times 3.143$$

$$\text{MDL} = 0.022 \text{ ng/mL}$$

15.2 Calculation of Stock Standard Concentration

The concentration in ng/mL is calculated below:

$$\text{Stock Concentration} = \frac{(\text{Volume Stock Added (mL)} \times \text{Working Standard (ng / mL)})}{\text{Total Volume (mL)}} \times \frac{1(\text{mL})}{1000(\mu\text{L})}$$

15.3 Calculation of Calibration and Check Standard Concentration

The concentration in the calibration, check standard and method spike standards is calculated below:

$$\text{Cal Std Conc.} = \frac{(\text{Volume Stock Added (mL)} \times \text{Stock Concentration (ng / mL)})}{\text{Total Volume (mL)}} \times \frac{1(\text{mL})}{1000(\mu\text{L})}$$

15.4 Calculation of Least Squares Linear Regression Calibration Curve

Use a Least Squares Linear Regression routine (using Chromeleon7 Client chromatography software) to calculate a correlation coefficient, slope, and intercept. Use concentration as the X-term (independent variable) and response as the Y-term (dependent variable).

15.5 Calculation of the Coefficient of Correlation

The correlation coefficient, R, is the square root of R² where:

$$R^2 = \frac{\left[\sum (XY) - \frac{\sum (X)\sum (Y)}{n} \right]^2}{\left[\sum (X^2) - \frac{(\sum X)^2}{n} \right] \left[\sum (Y^2) - \frac{(\sum Y)^2}{n} \right]}$$

15.6 Calculation of the Concentration of Cr⁶⁺ in Sample

The concentration in the sample is calculated below:

$$\text{Cr}^{6+} \text{ in Sample (ng/mL)} = \frac{\text{Sample Response} - \text{Intercept}}{\text{Slope}}$$

15.7 Calculation of ICV and CCV Percent Recovery

The ICV and CCV percent recovery is calculated below:

$$\text{Cr}^{6+} \text{ Percent Recovery} = \frac{\text{Concentration in CCV (ng/mL)}}{\text{Expected Concentration (ng/mL)}} \times 100$$

15.8 To calculate the concentration of Cr⁶⁺ in the air sampled, the volume of air sampled must be known.

$$\text{Cr}^{6+} \text{ Concentration (ng/m}^3\text{)} = \frac{C \text{ (ng/mL)} \times V_2 \text{ (mL)}}{V_1 \text{ (m}^3\text{)}}$$

where:

C	=	Concentration of Cr ⁶⁺ in analyzed sample
V ₁	=	Volume of air sampled
V ₂	=	Total volume of sample extract

15.9 Calculation of Laboratory Control Sample Recovery

Percent recoveries of the LCS and LCS duplicates are calculated as follows. First, the concentration of Cr⁶⁺ in the LCS is calculated as described in Section 15.5. The corrected weight of Cr⁶⁺ is divided by the amount of Cr⁶⁺ spiked and multiplied by 100 as shown below:

$$\text{LCS Cr}^{6+} \text{ Percent Recovery} = \frac{\text{Concentration in LCS (ng/mL)}}{\text{Spiked Concentration (ng/mL)}} \times 100$$

16.0 QUALITY CONTROL

Method Quality Objectives (MQO) and data assessment criteria, are determined from the results of the quality control samples. The MQO criteria is presented in Table 24-1.

16.1 Sample Collection Quality Control

All samples being logged in from the field are checked for these criteria. The quality control criteria for the filters are given below. If a sample that is being logged in from the field meets these criteria, it is considered invalid.

16.1.1 Filters dropped or contaminated with any foreign matter (i.e., dirt, finger marks, ink, liquids, etc.) are invalid.

16.1.2 Filters with tears or pinholes which occurred before or during sampling are invalid.

16.1.3 Sample flowrate:

C If the average flowrate is less than 9.0 LPM or exceeds 16 LPM, the filter is invalid.

C If the start and stop flowrates differ more than " 10%, the filter is invalid.

16.1.4 Filter samples collected by the samplers which operate less than 23 hours or more than 25 hours are invalid.

16.1.5 If a power failure occurs during a sample run which causes the stop time or sample duration requirements to be violated, the sample is invalid.

16.2 Initial Calibration

Run a calibration curve with a minimum of five-point as described in Section 13.0 after initially setting up the instrument and whenever the calibration check standard does not fall within the $\pm 15\%$ window. Initial calibration ranges from 0.1 to 2.0 ng/mL Cr⁶⁺. Calculate a correlation coefficient. If the correlation coefficient is less than 0.995, identify the cause and correct it. Repeat the calibration if necessary, or reinject any outliers that have been reprepared.

16.3 Initial Calibration Verification/Continuing Calibration Verification

Analyze initial calibration verification (ICV) after the calibration. Analyze a Continuing calibration verification (CCV) after every 10 samples and at the end of the sequence to verify instrument calibration. If the calibration check response is not within $\pm 15\%$ of expected response, determine the cause. The instrument may be malfunctioning, the check standard may not be valid, or the instrument may need to be recalibrated.

16.4 Initial Calibration Blank/Continuing Calibration Blank

Analyze an initial calibration blank (ICB) after the initial calibration and ICV. Analyze a continuing calibration blank (CCB) after every CCV and at the end of the sequence to verify that no contamination is occurring during the analysis. The acceptance criterion is less than the MDL.

16.5 Laboratory Control Sample (LCS)

Prepare a LCS for every 10 samples prepared to ensure there are no matrix effects from the filters. Spike 10 μL of the LCS spike solution onto an unused filter, dry in the Nitrogen purged glove box, and prepare and analyze with the rest of the samples. The acceptance criterion is 80-120% recovery. If the spikes are outside of these limits, check the calibration and extraction procedures.

16.6 Replicate Analysis

Replicate analyses should be performed on all duplicate samples received by the laboratory. The replicate analyses should be within $\pm 20\%$ greater than 3 times the MDL. If the replicate analyses are outside of these limits, verify that the peaks are integrated properly, that there is no interference from other components in the sample and that the instrument is working properly. This data should be flagged.

16.7 Method Detection Limit

The method detection limit (MDL) Described in Section 15.1

16.8 Retention Time

Retention times must be within ± 5 of the expected retention time in order to be identified as positive hits. If they vary by more than $\pm 10\%$ from check sample to check sample, stop the analysis, check for an instrument problem. If the retention times change from the beginning of the day to the end of the day, the system may be changing over the course of the day.

16.9 Performance Evaluation (PE) Samples

Performance evaluation samples should be obtained as available from independent sources and analyzed as a routine sample.

16.10 Control Charts

16.10.1 Retention Time

Chart the retention time. The retention time should not vary by more than $\pm 5\%$ of that on the calibration curve. If the retention time is out of control, check column, check the mobile phase delivery system for

leaks or plugs, and make sure the sample valve is properly aligned. Control charts should be updated daily or each time a check standard is analyzed whichever is least frequent.

16.10.2 Laboratory Control Samples

Chart the LCS. The LCS should not vary more than $\pm 20\%$ of the actual value. If the spikes are outside of these limits, check the calibration and extraction procedures.

17.0 POLLUTION PREVENTION

When possible, minimize the amount of chemicals used in the preparation and analysis of the Cr^{6+} filters to reduce waste.

18.0 CORRECTIVE ACTION

Corrective action for any Cr^{6+} analyses data quality issues should be developed by each laboratory. Table 24.1 gives the data quality guidelines and the associated recommended corrective actions.

19.0 WASTE MANAGEMENT

19.1 The eluent waste should be placed in an appropriately labeled waste container in the laboratory.

19.2 In the laboratory, there should be a satellite hazardous waste container for the Cr^{6+} working standards.

19.3 The analyst is responsible for contacting the hazardous waste personnel to dispose the waste.

20.0 MAINTENANCE

20.1 Daily maintenance

Rinse the IC piston before and after daily operation to prevent the build-up of salt crystals or other contaminants that will damage the piston seals (see instrument manual).

20.2 Periodic Maintenance

For regular periodic maintenance, see instrument manual.

20.2.1 The IC eluent manifold is flushed at the end of each day with DI water.

- 20.2.2 Check inside the chambers for leaks. Wipe up liquid spills and rinse dried reagents off with DI water.
- 20.2.3 Replace the slip-on filters every 1 to 2 months or when changing eluents (see instrument manual).
- 20.2.4 Replace the 20 μm filter media in the in-line filter holder every 1 to 2 months or when changing eluents.
- 20.2.5 The AGP requires regular lubrication every 3 to 6 months to keep the left piston operating smoothly (the right piston, however, requires no lubrication). Refer to the instrument manual for instructions.

21.0 SHORTHAND PROCEDURE

- 21.1 Prepare filters.
- 21.2 Send filters to site.
- 21.3 Receive filter samples.
- 21.4 Inspect filter samples.
- 21.5 Place filters in an extraction tube.
- 21.6 Add 10 mL of 20 mM Sodium Bicarbonate in DI water solution to the extraction tube.
- 21.7 Sonicate for 1 hour.
- 21.8 Calibrate IC.
- 21.9 Analyze the extracts by IC.

22.0 DOCUMENTATION AND DOCUMENT CONTROL

- 22.1 All information concerning sample preparation, standard preparation, instrument conditions, etc., must be written in the analyst's notebook.
- 22.2 The instrument calibration values, i.e., DI water conductance readings, separator column conductance, and both column conductances must be written in the IC notebook kept by the instrument. A list of the injections must be recorded in addition to the following information: type of eluent used, system number, type analysis, date of analysis, and retention time.

- 22.3 All calculations and the type of method for determining concentration must be recorded in the analyst's notebook. Any unusual problems or conditions must also be noted.
- 22.4 Record all maintenance performed on the instrument in the maintenance logbook for this particular instrument.
- 22.5 Record all sample injections, including quality control samples, performed by the instrument in the injection logbook for this particular instrument.

23.0 REFERENCES

DX-300 Series Chromatography System, and DX-300 Chromatography System Operator's Manual, Dionex Corporation, 117171.

Advanced Gradient Pump Operators Manual, Dionex Corporation, Document No. 034463, 117171.

CARB 039, Extraction and Analysis of Hexavalent Chromium by Ion Chromatography, 1993. A summary is found at <http://www.arb.ca.gov/aaqm/sop/summary/summary.htm>.

24.0 TABLES, DIAGRAMS, FLOWCHARTS, VALIDATION DATA

Table 24-1. Summary of Quality Control Procedures for Hexavalent Chromium Analysis

Parameter	Frequency	Acceptance Criteria	Corrective Action
Initial 5-point calibration standards	Before every sequence	Correlation coefficient 0.995	1) Repeat analysis of calibration standards. 2) Reprepare calibration standards and reanalyze.
Initial Calibration Verification (ICV)	Before every sequence, following the initial calibration	Recovery 85-115%	1) Repeat analysis of initial calibration verification standard. 2) Repeat analysis of calibration standards. 3) Reprepare calibration standards and reanalyze.
Initial Calibration Blank (ICB)	One per Batch, following the ICV	Below MDL	1) Reanalyze. 2) Reprepare blank and reanalyze. 3) Correct contamination and reanalyze blank. 4) Flag data of all samples in the batch.
Continuing Calibration Verification (CCV)	Every 10 samples and at the end of the analytical sequence	Recovery 85-115%	1) Repeat analysis of CCV. 2) Reprepare CCV. 3) Flag data bracketed by unacceptable CCV.
Laboratory Control Sample	One per 10 samples	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 < 20% for concentrations greater than 5 x the MDL.	1) Check integration 2) Check instrument function 3) Flag samples
Continuing Calibration Blank (CCB)	After every CCV and at the end of the sequence	Below MDL	1) Reanalyze. 2) Reprepare blank and reanalyze. 3) Correct contamination and reanalyze blank. 4) Flag data of all samples in the batch.

Figure 24-1. Flowchart for Hexavalent Chromium Samples

