METHOD 34

REF: Reg 11-8-301
11-8-310
11-8-330

DETERMINATION OF HEXAVALENT AND TOTAL CHROMIUM IN EFFLUENT SAMPLES FROM ELECTROLYTIC CHROME PLATING OPERATIONS

1) PRINCIPLE

1.1 This method applies to the determination of hexavalent chromium **(Cr^{+6})** and total chromium emissions from chrome plating operations.

1.2 Particulate emissions are collected from the source by use of Source Test Procedure ST-35. The collected samples, including the probe wash, are divided into two **(2)** equal portions with one portion used for total chromium analysis and the other portion for hexavalent chromium analysis.

1.3 For the total chromium analysis the sample is subjected to a hot nitric acid digestion and subsequent analysis by atomic absorption spectrophotometry **(AAS)**. The minimum detectable limit is 10 µg chromium per sample. The upper limit can be extended by appropriate dilution.

1.4 For the hexavalent chromium analysis, the sample is extracted in an alkaline solution and analyzed by the diphenylcarbazide colorimetric method. The minimum detectable limit is 8.0 µg Cr^{+6} per sample. The upper limit can be extended by appropriate dilution.

1.4.1 In order to prevent any conversion of hexavalent chromium to the trivalent form, the alkaline extraction must be performed within two **(2)** days after sample collection. Final color development must be completed within one week of the sample collection.

1.5 Molybdenum, mercury and vanadium at 20 mg levels can react with diphenylcarbazide to form colors which interfer with the Cr^{+6} analysis. Samples from chrome plating operations would, of course, not contain these metals.

2) APPARATUS

2.1 Analysis of Hexavalent Chromium using Diphenylcarbazide Colorimetric Method.

2.1.1 Fisher Filtrator. Available from Fisher Scientific. **Cat. #09-788.**

2.1.2 Fisher Aireject Aspirator. Available from Fisher Scientific. **Cat. #09-956.**

2.1.3 Volumetric Flasks. Assorted sizes as needed.

2.1.4 Pipettes. Assorted sizes as needed.

2.1.5 Spectrophotometer. Capable of measuring absorbance at 540 nm.

2.1.6 Funnel with Fritted Disc. Available from Curtin Matheson Scientific. **Cat. #101-403.**

2.1.7 Vari Whirl Mixer.

2.1.8 Refrigerator.

2.1.9 Brown Bottle with Screw Cap. Assorted sizes as needed.

2.1.10 Burrell Wrist Action Shaker.

2.1.11 Parafilm.

2.1.12 25 ml Graduated Test Tube.

2.1.13 Graduated Erlenmyer Flasks. Assorted sizes as needed.

2.1.14 Graduated Cylinders. Assoprted sizes as needed.

2.1.15 180^{o}C Surface Temperature Thermometer.

2.1.16 Spin Bar 1-5/8" x 3/4".

2.1.17 Hotplate Stirrer, Magnetic. Available from Lab-Line.

2.1.18 Disposable Pipette.

2.2 Analysis of Total Chromium using Atomic Absorption Spectrophotometry (AAS).

2.2.1 Atomic absorption spectrophotometer. This unit is fitted with a compatible data station and printer/plotter.

2.2.2 Chromium Hollow Cathode Tube.

2.2.3 Hot Plate with Variable Settings.

2.2.4 Beakers. Assorted sizes as needed.

2.2.5 50 ml Volumetric Flasks.

2.2.6 250 ml Phillips Beakers.

2.2.7 65 mm Watchglass.

2.2.8 Whatman #1 Filter Paper.

2.2.9 Glass Rod.

2.2.10 180^{o}C Surface Temperature Thermometer.

NOTE 1: Glassware - Borosilicate glassware should be used throughout the analysis.

3) REAGENTS

3.1 Concentrated Nitric Acid, HNO_3, (69-71%)

3.2 Dilute Nitric Acid, (0.1 N). Pipet 6.3 ml of concentrated HNO_3 to 1 l graduated Erlenmayer flask half full of distilled water. Mix the solution, add distilled water to the mark, and remix thoroughly.

3.3 Potassium Dichromate ($K_2Cr_2O_7$) Reagent Grade.

3.4 Acetone. Spectroscopic Grade.

3.5 Distilled Water.

3.6 **0.1% $KMnO_4$ Solution.** Dissolve 0.1 g of postassium permanganate **($KMnO_4$)** in 100 ml of distilled water. Store in a tightly capped brown glass bottle.

3.7 **Extraction Reagent (2% NaOH/3% Na_2CO_3)**. Dissolve 20 g NaOH pellets and 30 g anhydrous Na_2CO_3 in 1 l of distilled water. Store the solution in a tightly capped polyethylene bottle. Prepare fresh monthly.

3.8 **6 N H_2SO_4.** Carefully add 166 ml of concentrated sulfuric acid to about 600 ml of distilled water in a 1 l volumetric flask. Mix well, cool to room temperature and dilute to the mark with distilled water.

3.9 **0.25% 1, 5-Diphenylcarbazide Solution.** Dissolve 0.5 g of **1, 5-**diphenylcarbazide in 100 ml of acetone in a 250 ml beaker. Dilute the solution to 200 ml with distilled water **(NOTE 2)**. Transfer the solution to a brown bottle, cap tightly and keep in the refrigerator. The solution is stable for at least one month.

3.10 **Cylinder Nitrogen.**

NOTE 2: **Dissolve the 1, 5-Diphenylcarbazide in acetone alone, then add the water. Diphenylcarbazide does not dissolve well in acetone - water mixture.**

4) ANALYTICAL PROCEDURE FOR DETERMINING HEXAVALENT CHROMIUM USING THE DIPHENYLCARBAZIDE COLORIMETRIC METHOD

4.1 Cleaning of Glasswares (NOTE 3).

4.1.1 Glasswares should be soaked in warm, mild detergent solution to remove any residual grease or chemicals.

4.1.2 After the initial cleaning **(4.1.1)** the glassware must be soaked in 2 N HNO_3 for 1-2 hrs. Rinse thoroughly with distilled water and dry in the oven.

4.1.3 For glassware that has been previously cleaned as in Section **4.1.1**, simply procede with the HNO_3 treatment outlined in Section **4.1.2**.

NOTE 3: **Never use chromic acid cleaning solution to clean the glassware.**

4.2 Removal of Reducing Agents in the Extraction Reagent (3.7) and Dilute Sulfuric Acid Solution (3.8). These solutions may contain small amount of reducing agents that can react with hexavalent chromium.

4.2.1 Place the flask containing the extracting reagent on a magnetic stirrer **(2.1.17).** Put a spin bar in the flask and turn on the magnetic stirrer. Add 2 ml of 0.1% $KMnO_4$ solution using a 5 ml pipette, to the flask. Wait a few seconds. If the reagent remains colorless, continue the addition of the permanganate solution, dropwise, using a disposable pipette **(2.1.18)**, until a very faint pink color is attained. This indicates that an excess of potassium permanganate has been added, thus neutralizing the reducing agent present in the extraction reagent. Cover the flask.

4.2.2 Repeat Section 4.2.1. with the 6 N H_2SO_4 solution. However, instead of adding 2 ml of 0.1% $KMnO_4$ solution initially to the flask, add 0.75 ml instead.

4.3 Sample Preparation. For Hexavalent chromium the procedure from **4.3.1** thru **4.3.6** must be performed within two days after sample collection to prevent and/or minimize any conversion of hexavalent chromium to the trivalent state.

4.3.1 Transfer from its container one-half of the acetone probe wash to a 125 ml Phillips beaker A and the other half to another Phillips beaker B. Rinse the container with acetone. Transfer half of the rinse to beaker A and the other half to beaker B. Evaporate both beakers down to about 5 ml on a hot plate, which is maintained at about 80^{o}C surface temperature. Take the beakers off the hot plate and complete the evaporation of acetone by flushing the beakers with nitrogen gas. Save beaker A for hexavalent chromium determination and beaker B for total chromium determination.

4.3.2 Take the filter from its container and divide it into quarters. Take the two **(2)** quarters that are diagonal to each other and cut them up into small pieces, approximately one-half inch square. Save the other 2 quarters for total chromium determination.

4.3.3 Place the cut up filter pieces in a 125 ml Phillips beaker. Add 25 ml of the extraction reagent **(Section 3.7).** Cover the beaker with parafilm and shake the solution at room tempeature for 30 minutes, using the Burrell wrist action shaker.

4.3.4 Assemble the Fisher Filtration Apparatus.

4.3.4.1 Place a 100 ml volumetric flask **(receiving flask)** on the rubber padded platform.

4.3.4.2 Place the glass bell over the receiving flask and hold in place with the wire bail.

4.3.4.3 Attached a rubber stopper to the stem of the funnel **(Section 2.1.6).** Connect the funnel to the glass bell.

4.3.4.4 Connect the assembled filtration apparatus to the water aspirater. **(Section 2.1.2).**

4.3.5 Pour the alkaline extract into the funnel and turn on the water to start the vacuum filtration. Wash the filter with approximately 40 ml of distilled water using 10 ml aliquots. Turn off the Fisher filtrator then the water aspirator. Remove the receiving flask from the filtration apparatus.

4.3.6 To the evaporated acetone probe wash in beaker A **(Section 4.3.1)** add 10 ml of distilled water. Swirl, set stand a few minutes and transfer to the 100 ml volumetric flask contents from **Section 4.3.5.** Repeat the above water washing one more time.

4.3.6.1 The sample is now stable and may be stored for five **(5)** days prior to color development and quantitation.

4.3.7 Color Development.

4.3.7.1 Slowly add 7.8 ml of 6 N H_2SO_4 solution to the filtrate in the volumetric flask. Swwirl the solution to release the carbon dioxide gas. The PH of this solution is approximately 1.

4.3.7.2 **Add 2 ml Diphenylcarbazide Solution to the Acidified Filtrate (Section 4.3.6).** Swirl the solution until a pink/purple color is formed. Add distilled water to the mark. Cap the flask and mix the solution thoroughly. Allow the solution to stand about 10 minutes for full color development, but not more than an hour.

4.3.7.3 Read the absorbance of the sample at 540 nm using a half inch cuvette, after setting the spectrophotometer to zero absorbance with a reagent blank.

4.3.7.4 For each set of samples analyzed, treat an identical amount of unused acetone and filter disc as in Sections **4.3.1** thru **4.3.8**. Subtract the absorbance of the blank from the absorbance of the sample to obtain a net absorbance reading.

4.3.7.5 Determine the amount of hexavalent chromium in the sample from the standard curve derived in **Section 5.**

4.3.7.6 Samples with absorbance values greater than the working range of the standard curve must be diluted with a reagent blank and reanalyzed. Record the dilution factor, **(DF)**.

5) PREPARATION OF STANDARD CURVE FOR HEXAVALENT CHROMIUM.

5.1 **Chromium Standard Stock Solution.** Either procure a certified aqueous standard from a supplier **(Eg. Spex Industries, Alpha Products, or Fisher Scientific)** and verify by comparison with a second standard, **or** dissolve 2.829 g of Potassium Dichromate **($K_2Cr_2O_7$, analytical reagent grade)** in distilled water and dilute to 1 liter, in a 1 l volumetric flask. Stopper the flask and mix the solution thoroughly by inverting the flask several times. This solution contains 1000 µg Cr^{+6}/ml.

5.2 **Chromium Standard Working Solution.** Pipet 1 ml of the chromium stock standard solution into a 100 ml volumetric flask and dilute to the mark with distilled water. This solution contains 10 µg Cr^{+6}/ml. Stopper the flask and invert several times to mix the solution thoroughly. This working solution is always prepared fresh prior to use.

5.3 Add 25 ml of the extraction solution, previously treated with dilute $KMnO_4$ solution, **(Section 4.2)**, to each of a series of 100 ml volumetric flasks.

5.4 Add to each flask 0, 0.4, 0.8, 1.0, 2.0, 4.0, 6.0 and 8.0 ml of the chromium working standard solution **(5.2)**. These flasks respectively contain 0, 4.0, 8.0, 10.0, 20.0, 40.0, 60.0 and 80.0 µg Cr^{+6}.

5.5 Add slowly 7.8 ml of 6 N H_2SO_4 to each flask and shake well to remove the carbon dioxide gas. Do not cap the flasks while shaking.

5.6 Add 2 ml diphenylcarbazide solution to each flask, and dilute to the mark with distilled water. Cap the flasks and mix thoroughly by inverting the flasks several times. Allow at least 10 minutes for full color development but not more than 1 hour.

5.7 Read the absorbance of each standard in a 1/2" cuvette at 540 nm after setting the instrument to zero with the reagent blank.

5.8 Plot absorbance vs µg Cr^{+6}/100 ml using linear graph paper.

6) ANALYTICAL PROCEDURE FOR DETERMINATION OF TOTAL CHROMIUM USING ATOMIC ABSORPTION SPECTROPHOTOMETRY (AAS).

6.1 Clean the glassware to be used for total chromium as in **Section 4.1.**

6.2 Sample Preparation.

6.2.1 Cut up the remaining two **(2)** quarters of the filter disc into small pieces, approximately one half inch square, and put them in beaker B **(Section 4.3.1.)**

6.2.2 Prepare a filter and acetone blank with each batch of samples being analyzed for total chromium.

6.2.3 Add 10 ml of concentrated HNO_3 to each of the samples and blank. Cover each beaker with a ribbed watch glass.

6.2.4 Place the beakers on a hot plate that has a surface temperature of about 80°C. Reflux until the acid volume is reduced to about 5 ml. Then add another 5 ml concentrated HNO_3 to each beaker to complete the digestion. Continue to reflux the sample until the final volume is down to 1-2 ml.

6.2.5 Wash down the beaker walls and watch glass with distilled water. Filter the extract through a Whatman #1 filter paper to remove any insoluble materials.

6.2.6 Set the instrument parameters to obtain maximum sensitivity at a wave-length of 357.9 nm and a lamp current of 10 ma. Use an air acetylene flame.

6.2.7 Aspirate the blank and each sample into the flame and record the respective absorbance values. **(NOTE 4)**.

NOTE 4: A compatible data station with a printer can provide a printout of the standard curve and Cr concentration (ppm) in the sample.

6.2.8 Samples that have absorption values higher than the working range of the standard calibration curve must be diluted with dilute nitric acid **(3.2)** to be within the working range of the standard curve. Record the dilution factor, **(DF)**, required to have the sample**(s)** in the working range.

6.2.9 Standards should be aspirated after every fourth or fifth sample to insure instrument response has not changed.

7) PREPARATION OF STANDARD CURVE FOR TOTAL CHROMIUM

7.1 Use the Chromium Standard Stock Solution from Section 5.1.

7.2 Working Standard Chromium Solution. At least five individual standards normally in the range of 0 to 2.5 µgm Cr/ml in dilute nitric acid are prepared by appropriate dilution of the standard stock solution **(5.1)**. Working standards must be prepared fresh prior to use.

7.2.1 Prepare a standard curve on linear graph paper by plotting absorbance of the individual standards vs µg Cr/ml. **(NOTE 4)**.

8) CALCULATION

8.1 Total Hexavalent Chromium in a Sample.

$$\text{Total } \mu g\ Cr^{+6} = \mu g\ Cr^{+6}/100\ ml \times 2 \times DF$$

Where:

$\mu g\ Cr^{+6}/100$ ml = Amount of Cr^{+6} found in Section 4.3.10.

2 = Aliquot Factor (1/2 total sample is used)

DF = Dilution Factor (Section 4.3.11). If there is no sample dilution, DF, = 1

8.2 Total Chromium in the sample.

8.2.1 Net µg Cr/ml in each sample is equal to µg Cr/ml in the sample less the µg Cr/ml in the blank **(Section 6.2.7)**.

8.2.2 Total µg Cr/sample = **(8.2.1)** x 50 x 2 x DF

Where: 50 = Total volume of extract used of the analysis for total chromium

2 = Aliquot factor (1/2 of sample is used).

DF = Dilution factor (Section 6.2.9). If no dilution is made, DF = 1.

9) REFERENCES

9.1 Determination of Total Chromium and Hexavalent Chromium Emissions from Stationary Sources. ARB Method 425.

9.2 Tentative Method of Analysis for Chromium Content of Atmospheric Particulate Matter by Atomic Absorption Spectroscopy. Method 312. Second Edition. ALPHA American Public Health Association.