HEXAVALENT CHROMIUM

Method Number:	ID-103
Matrix:	Air
OSHA Permissible Exposure Limits Chromic acid and chromates as CrO_3 (Final Rule Limit):	0.1 mg/m^3 (Ceiling)
Chromic acid and chromates as CrO_3 (Transitional Limit):	0.1 mg/m^3 (Time Weighted Average)
Collection Device:	An air sample is collected on a 37-mm diameter polyvinyl chloride filter (5-µm pore size) using a calibrated personal sampling pump.
Recommended Sampling Rate:	2 L/min
Recommended Air Volume Range:	30 to 960 L
Analytical Procedure:	The chromium (VI) is extracted from the filter using a carbonate/bicarbonate buffer solution and then analyzed by differential pulse polarography.
Detection Limits Qualitative:	0.006 mg/m^3 as CrO_3 (30-L air sample)
Quantitative:	0.019 mg/m^3 as CrO_3 (30-L air sample)
Precision and Accuracy Validation Range:	0.1 to 0.6 mg/m³ as CrO_3 (30-L sample)
CV_1 Range:	0.012 to 0.019
Bias Range:	+0.012 to +0.053
Overall Error Range:	±2.7 to ±8.7%
Method Classification:	Validated Method
Chemist:	James Ku
Date (Date Revised):	1982 (February, 1990)

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1. Introduction

This method describes the air sampling and subsequent analysis of workplace exposures to chromic acid and chromate compounds. Analysis is conducted by differential pulse polarography (DPP).

1.1 History

This method has been developed at the OSHA Salt Lake City Technical Center (OSHA-SLTC) to improve the determination of chromic acid and chromates [as total Cr(VI)] by minimizing interferences and offering increased sensitivity.

The classical method of Cr(VI) analysis is colorimetry using s-diphenylcarbazide (DPC) after acid extraction of the Cr(VI) from the sample (8.1, 8.2). This method is unsatisfactory for determining certain insoluble chromate compounds (8.3) and also has interferences from many heavy metals (8.2). Reducing agents, such as Fe(II), could convert the Cr(VI) to Cr(III) in the acidic extraction medium used (8.4).

The extraction of Cr(VI) in basic solution and subsequent analysis by colorimetry using DPC has been reported (8.3). The extraction technique used in this method is a modification of that suggested in Reference 8.3.

In this method the analytical technique for Cr(VI) is DPP. Polarographic techniques have been previously reported for the analysis of chromium species (8.5, 8.6).

1.2 Principle

1.2.1 An air sample is collected on a 37-mm polyvinyl chloride (PVC) filter [Note: Cellulose ester filters are unacceptable because they may react with and reduce the hexavalent chromium [Cr(VI)] species (8.7-8.9)]. The filter is treated with a hot 10% sodium carbonate / 2% sodium bicarbonate buffer solution to extract the Cr(VI) from the sample and to protect against reduction to Cr(III). The Cr(VI) in the extract is analyzed by DPP using a dropping mercury electrode.

1.2.2 The reaction between chromates and carbonate is illustrated by the following equation (8.3):

$$MCrO_4 + CO_{3(2-)} \text{----->} MCO_3 + CrO_{4(2-)}$$

where M = metals (i.e., lead, zinc, cadmium, ...)

In the presence of a large excess of carbonate, equilibrium is quantitatively shifted to the right. The chromate compounds (soluble and insoluble) are converted to their corresponding carbonates.

1.3 Advantages and Disadvantages

1.3.1 The analysis is specific for Cr(VI) in the presence of Cr(III). Other reducing substances, such as magnetite (Fe_3O_4) do not appear to significantly interfere (8.8).

1.3.2 In addition to the Cr(VI) analysis, it is possible to determine other soluble compounds such as lead and zinc salts in the same solution.

1.3.3 By using alkaline extraction conditions (pH 10 to 11), sample recovery is improved by preventing Cr(VI) losses which may occur in a more acidic extraction media. Both water soluble and insoluble Cr(VI) compounds are soluble in this alkaline extraction medium.

1.3.4 The sensitivity is adequate for measuring workplace atmospheric concentrations of Cr(VI) and is less sensitive to interferences noted when using the colorimetric/DPC procedure (8.2, 8.7). Potential interferences with the polarographic determination may be rendered insignificant by altering analytical conditions such as changing the supporting electrolyte solution.

1.3.5 Polarographic instruments have a wide analytical range. This diminishes the need for withdrawing aliquots or diluting the samples in order to be within the linear analytical range of the instrument.

1.3.6 A disadvantage is the polarographic instrument may not be available in some analytical laboratories; however, the extracted samples may be acidified and then analyzed using a modified colorimetric/DPC method (please see Section 7 of Reference 8.8 for further information). Spiked samples using compounds known to be present in the sample matrix

should be taken through this alternate procedure first to determine if any loss of Cr(VI) occurs during acidification. Detection limits should also be determined.

1.4 Uses

Occupations having a potential exposure to compounds containing Cr(VI) as well as a list of different chromate compounds are listed in Reference 8.10.

2. Range and Detection Limit (8.8)

2.1 This method was validated using insoluble and soluble chromate compounds. The compounds used were lead, zinc, calcium, and potassium chromates. Filter samples were spiked with about 2 to 9 µg [as Cr(VI)], prepared, and then diluted to 10-mL sample solution volumes. Using 30- or 840-L air volumes, these spiked samples would give an approximate concentration range of:

30-L air sample	0.1 to 0.6 mg/m³ as CrO_3
840-L air sample	0.005 to 0.02 mg/m³ as CrO_3

This method has the sensitivity necessary to determine compliance with either the OSHA Transitional or the Final Rule PEL. Samples for Final Rule determinations should be taken with at least 30-L air volumes.

2.2 The qualitative and quantitative detection limits for 10-mL sample solution volumes were 0.19 µg and 0.58 µg as CrO_3, respectively.

3. Method Performance (8.8)

The DPP analytical method has been evaluated using a time weighted average concentration of 0.009 mg/m³ as CrO_3 (840-L air sample).

3.1 The pooled analytical coefficients of variation (CV_1) and recoveries at 0.5, 1, and 2 times this concentration for specific chromate compounds were:

Compound	CV_1	Recovery
Lead chromate ($PbCrO_4$)	0.012	100.3%
Zinc chromate ($4ZnO\bullet CrO_3.3H_20$)*	0.017	105.3%
Calcium chromate ($CaCrO_4$)	0.015	101.9%
Potassium chromate (K_2CrO_4)	0.019	101.2%

*Molecular formula was confirmed by X-ray diffraction (8.8)

3.2 A comparison of methods using spiked samples containing $PbCrO_4$ showed that results obtained by a modified colorimetric/DPC method were duplicated for the DPP method. There was no significant bias between the two methods (8.8).

3.3 A collection efficiency of 0.945 ± 0.035 has been previously determined for chromic acid mist collected on PVC filters (8.11).

3.4 Quality control samples were prepared by spiking aqueous solutions of potassium dichromate on PVC filters. These samples were analyzed along with survey samples at OSHA-SLTC from 1982 to 1989. The following results were obtained (8.12):

Samples (N)	282
Average recovery	94.1%
CV_1	0.10

4. Interferences

4.1 Reducing species such as Cr(III) or magnetite (Fe_3O_4) in an excess of 10:1 or 50:1, respectively, over Cr(VI) did not produce a significant interference with this method (8.8).

4.2 The effect of many interferences can be minimized by changing the operating conditions of the polarograph. Additional polarographic confirmation of a cation in a sample may be performed in a second electrolyte and observing if the new half-wave potential is consistent with the determination made using the first electrolyte.

5. Sampling

5.1 Sampling Equipment (Note: Bulk samples can be collected and analyzed. **Filter or wipe samples collected on cellulose or cellulose esters are unacceptable** due to chromate species instability on these media.)

5.1.1 Sample assembly:

a) Filter holder consisting of a two- or three-piece cassette, 37-mm diameter.
b) Backup pad, 37-mm, cellulose.
c) Membrane filter, PVC, 37-mm, 5-µm pore size [part no. 625413, Mine Safety Appliances (MSA), Pittsburgh, PA or cat. no. P-503700, Omega Specialty Instrument Co., Chelmsford, MA).

5.1.2 Gel bands (Omega Specialty Instrument Co., Chelmsford, MA) for sealing cassettes.

5.1.3 Sampling pumps capable of sampling at 2 L/min.

5.1.4 Assorted flexible tubing.

5.1.5 Stopwatch and bubble tube or meter for pump calibration.

5.1.6 Scintillation vials (for bulk samples), 20-mL, part no. 74515 or 58515, (Kimble, Div. of Owens-Illinois Inc., Toledo, OH) with polypropylene or Teflon cap liners.

5.2 Sampling Procedure

5.2.1 Place a PVC filter and a cellulose backup pad in each two- or three-piece cassette. Seal each cassette with a gel band.

5.2.2 Calibrate each personal sampling pump with a prepared cassette in-line to approximately 2 L/min.

5.2.3 Attach prepared cassettes to calibrated sampling pumps (the backup pad should face the pump) and place in appropriate positions on the employee or workplace area. Collect the samples using a total air volume of at least 30-L.

5.2.4 For Time Weighted Average samples: If the filter becomes overloaded while sampling, consecutive samples using shorter sampling periods should be taken.

5.2.5 Wipe samples can be taken using PVC filters as the wipe media. Wear clean, impervious, disposable gloves when taking each wipe sample. If possible, wipe a surface area covering 100 cm^2. Fold the wipe sample with the exposed side in and then transfer into a 20-mL scintillation vial.

5.2.6 If bulk samples are necessary, collect the bulk samples using a grab sampling technique suitable for the particular material(s) in use. If possible, transfer any bulk samples into 20-mL scintillation vials.

5.3 Shipment

5.3.1 Place plastic end caps on each cassette after sampling. Submit at least one blank sample with each set of air samples. Blank filter samples should be handled in the same manner as other samples, except no air is drawn through the blank. Attach an OSHA-21 seal around each cassette in such a way as to secure the end caps. Send the samples to the laboratory with the OSHA 91A paperwork requesting chromate analysis.

5.3.2 Seal scintillation vials with vinyl or electrical tape. Securely wrap an OSHA-21 seal length-wise from vial top to bottom.

5.3.3 Bulk samples should be shipped separately from air samples. They should be accompanied by Material Safety Data Sheets if available. Check current shipping restrictions and ship to the laboratory by the appropriate method.

6. Analysis

6.1 Safety Precautions

6.1.1 Certain chromate compounds have been identified as suspected carcinogens (8.10). Care should be exercised when handling these compounds.

6.1.2 When handling <u>any</u> chemicals, a labcoat, safety glasses or goggles, and gloves should be worn.

6.1.3 The buffer/extraction/electrolyte (BEE) solution is basic and somewhat corrosive. Clean up any spills immediately. This solution should be stored in polyethylene bottles since precipitated salts form readily during evaporation and will cause glass stoppers to seize. Samples prepared in glassware should be analyzed and properly disposed of as soon as possible.

6.1.4 Mercury is used as the working electrode in DPP. Always exercise caution to prevent any potential spills of mercury. Containment vessels should surround the polarograph and spill control devices should be available when handling or working with mercury.

6.1.5 Refer to the Standard Operating Procedure (SOP) (8.13) and instrument manuals for proper operation of the polarographic instrument and safety precautions.

6.1.6 **<u>Extra care</u>** should be used when handling perchloric acid ($HClO_4$). Perchloric acid should only be used in a hood that has been approved for $HClO_4$ use. In this hood:

a) Organic reagents should not be used.
b) A water washdown system for the ducts and work surface is installed and periodically used.
c) Precautions should be taken to ensure that explosions or spontaneous ignition of sample material from $HClO_4$ is prevented.

Working with $HClO_4$ is very hazardous. Be sure to wear safety glasses, a labcoat, and gloves. Always add nitric acid (HNO_3) with $HClO_4$ when digesting samples. Watch the samples during $HClO_4$ digestion carefully since there is a chance they could ignite. Always keep HNO_3 nearby when using $HClO_4$. In the event of sample media ignition, quickly douse the sample with a small portion of HNO_3.

6.2 Equipment

6.2.1 Polarographic Analyzer or Controller, Model 384 or 384B, (Princeton Applied Research, Princeton, NJ), with a Model 303 or 303A dropping mercury electrode.

6.2.2 Glass polarographic cells, 15-mL.

6.2.3 Nitrogen purification system: Gas purifier for deoxygenating nitrogen, [(Oxiclear, part no. DGP-250, Labclear, Oakland, CA). As an alternative, an oxygen scrubber can be constructed using a vanadous chloride solution as described in reference 8.14].

6.2.4 Hot plate and exhaust hood.

6.2.5 Phillips beakers, borosilicate, 125-mL, with watch glass covers.

6.2.6 Filtration apparatus: Vacuum, vacuum flask, and PVC filters, 5-µm pore size, 37 mm diameter.

6.2.7 Teflon-coated magnetic stirring bar and stirrer.

6.2.8 Analytical balance (0.01 mg).

6.2.9 Polyethylene bottles, 100-mL to 1-L size.

6.2.10 Volumetric and micropipettes, volumetric flasks, beakers, and general laboratory glassware. **Do not use** glassware for sample analysis of chromate compounds if it was:

1) previously cleaned with chromic acid cleaning solution
2) previously used for storage of chromium (VI) standards
3) previously used for storage of bulks containing high concentrations of chromium (VI)

6.3 Reagents - All chemicals should be reagent grade or better.

6.3.1 Nitrogen gas.

6.3.2 Deionized water (DI H_2O) with a specific conductance of less than 10 µS.

6.3.3 Sodium carbonate (Na_2CO_3), anhydrous.

6.3.4 Sodium bicarbonate ($NaHCO_3$).

6.3.5 Buffer/extraction/electrolyte (BEE) solution (pH approximately 10.5): Dissolve 100 g of Na_2CO_3 and 20 g of $NaHCO_3$ in about 500 mL DI H_2O contained in a 1-L volumetric flask. A Teflon-coated magnetic stirring bar and stirrer will facilitate dissolution. Rinse and remove the stirring bar and then dilute to the mark with DI H_2O. Transfer and store this solution in a tightly capped polyethylene bottle. Prepare monthly.

6.3.6 Potassium dichromate ($K_2Cr_2O_7$), or potassium chromate (K_2CrO_4).

6.3.7 Cr(VI) Stock Standard (1,000 µg/mL): Dissolve 2.829 g $K_2Cr_2O_7$ or 3.735 g K_2CrO_4 in DI H_2O and dilute to the mark in a 1-L volumetric flask. Prepare this solution every six months.

6.3.8 Cr(VI) standard (100 µg/mL): Dilute 10 mL of the Cr(VI) stock standard to 100 mL with DI H_2O. Prepare this solution every three months.

6.3.9 Cr(VI) working standard (10 µg/mL): Dilute 10 mL of the Cr(VI) 100 µg/mL standard to 100 mL with the BEE solution. Transfer to a polyethylene bottle. Prepare this solution daily.

6.3.10 Cr(VI) working standard (1 µg/mL): Dilute 10 mL of the Cr(VI) 10 µg/mL working standard to 100 mL with the BEE solution. Transfer to a polyethylene bottle. Prepare this solution daily.

6.3.11 Nitric acid (HNO_3), concentrated (69 to 71%).

6.3.12 Nitric acid 6 M: Carefully dilute 384 mL of concentrated (conc.) HNO_3 to 1 L using DI H_2O.

6.3.13 Nitric acid, 10% (v/v): Carefully dilute 100 mL of conc. HNO_3 to 1 L using DI H_2O.

6.3.14 Perchloric acid ($HClO_4$), conc. (69 to 71%).

6.3.15 Hydrogen peroxide (H_2O_2), 30%.

6.3.16 Mercury, triple distilled, for the working electrode.

6.4 Sample Preparation

6.4.1 Wash all glassware in hot water with detergent and rinse with tap water, 10% HNO_3, and DI H_2O (in that order). **Under no circumstances should chromic acid cleaning solutions be used.**

6.4.2 Adjust the hot plate to a temperature below the boiling point of the BEE solution.

6.4.3 If bulk samples are submitted, weigh out a representative aliquot of each bulk on separate blank PVC filters.

6.4.4 Carefully remove the PVC filter from the cassette or balance, place it face-down in a 125-mL Phillips beaker, and add 5 mL of BEE solution. Cover the beaker with a watch glass and heat the solution on the hot plate, with occasional swirling for 30 to 60 min. Allow extra extraction time for heavily loaded samples taken from spray paint operations. **Do not allow any solutions to boil or evaporate to dryness**. Conversion of Cr(VI) to Cr(III) can occur from excess heat (8.4).

6.4.5 Allow the solutions to cool to room temperature. Quantitatively transfer each solution to a 10- or 25-mL volumetric flask using BEE solution rinses. Dilute to volume with the BEE solution. Use 10-mL sample volumes for samples taken to determine if exposures exceed the OSHA Ceiling Permissible Exposure Limit for chromate.

6.4.6 If the solution is cloudy and/or other metal analyses are desired, filter the solution through a PVC filter in a vacuum filtration apparatus. If necessary, prepare and analyze samples for other metals using the appropriate techniques. An example would be to determine the total metal content of the sample residue by atomic absorption or inductively coupled plasma spectroscopy.

6.4.7 For samples taken from spray painting operations, digest the extracted filters containing the paint residue according to the following procedure:

Note: Evidence indicates base extractions are capable of recovering Cr(VI) in specific paint matrices (8.4). Due to the resistant properties of some industrial paints, an additional digestion is used for samples collected during spray painting to assure complete recovery of all Cr(VI).

1) After the extraction solutions are transferred to volumetric flasks and diluted to volume, place the sample beakers containing the remaining paint residue and any blanks in an exhaust hood. Carefully add 5 to 10 mL of conc. HNO_3 to each beaker. Place the beakers on a hot plate and heat the samples until about 1 mL remains.

2) Add 2 mL of conc. $HClO_4$ along with a second portion of 2 mL HNO_3, heat each sample, and then remove when about 1 mL remains. (Note: Please see Section 6.1.6 before using $HClO_4$.)

3) Add 1 or 2 mL of 30% H_2O_2 to the cooled solution to reduce any remaining Cr(VI). Let the sample sit for several min and then heat for approximately 5 min to boil off the H_2O_2. Allow the samples to cool to room temperature.

4) Dilute each digested sample to a 25 mL final volume with DI H_2O. Analyze these samples for chromium by atomic absorption using the procedure mentioned in Reference 8.15.

6.5 Standard Preparation

Prepare a series of Cr(VI) standards in the analytical range of 0.050 to 10 µg/mL. Make appropriate serial dilutions of the Cr(VI) working standards with the BEE solution.

6.6 Analytical Procedure

6.6.1 Cleaning equipment:

Soak polarographic cells in 6 M HNO_3 (preferably overnight), rinse thoroughly with DI H_2O, and air-dry. Errors occurring from the adsorption of chromium on the walls of glassware and analytical reagent contamination with chromium have been reported (8.16, 8.17). Therefore, take special precautions and also analyze a reagent blank using identical treatment as the samples.

6.6.2 Set the operating conditions for the instrument as follows (Note: If other types of instruments are used, refer to their operating and service manuals for comparable settings):

Analytical technique:	DPP
Initial potential:	-0.100 V
Final potential:	-0.450 V
Peak potential:	-0.300 V*
Nitrogen purge:	30 to 240 s
Scan increment:	2 mV
Pulse height:	0.050 to 0.080 V
Drop time:	1 s
Drop size:	medium or large

* Varies slightly - Dependent on instrument and sample conditions

6.6.3 Refer to Reference 8.13 or other instrument manuals for operating procedures.

6.6.4 Transfer a sample or blank to a polarographic cup. If the final solution volume was 10-mL, transfer the entire sample; if 25-mL, transfer a 10-mL aliquot. Transfer 10 mL of each standard into separate polarographic cups.

6.6.5 Purge each standard, blank, or sample between 30 to 240 s with purified nitrogen.

6.6.6 Analyze the reagent blank (10 mL of BEE solution), the standards, and the samples by measuring the peak current (nA). A standard should be analyzed after every five or six samples.

6.6.7 Wash the polarographic electrodes thoroughly with DI H_2O after each sample is analyzed.

6.6.8 Record the peak current (nA) and potential for each determination. A differential pulse polarogram of Cr(VI) in the BEE solution should display a peak at approximately -0.300 V when using the conditions described. A polarogram of a 1 µg/mL standard is shown in Figure 1.

6.6.9 If the peak current from a sample is above the largest standard used, an aliquot should be taken from the sample and diluted to 10 mL with BEE solution and analyzed. A dilution factor for this sample is applied when calculating results (Section 7.2).

6.6.10 Other metals such as lead and zinc may be determined in the same solution if required. Approximate peak potentials of -0.630 V for Pb and -1.350 V for Zn were found when these species were present in the BEE solution.

7. Calculations

7.1 Use a least-squares regression program to plot a concentration-response curve of peak current vs. concentration (µg/mL of standards). Determine the concentration (µg/mL) of each sample and blank from the curve.

7.2 Determine the air concentration of CrO_3 in each extraction sample according to the following equation:

$$C = \frac{[(A \times SA \times D \times GF) - (B \times SB \times GF)]}{Air\ Vol}$$

Where:

C = mg/m^3 CrO_3
A = amount of Cr(VI) in the sample solution (µg/mL)
B = amount of Cr(VI) in the blank solution (µg/mL)
SA = sample solution (mL)
SB = blank solution (mL)
D = dilution factor (if any)
GF = gravimetric factor used to convert the amount of Cr(VI) to CrO_3, GF = 1.923
Air Vol = air volume sampled (L)

7.3 For digested spray paint samples analyzed according to OSHA Method No. ID-121, the calculations above may be used without the gravimetric factor or use calculations mentioned in that method to determine the amount of total chromium.

7.4 For bulk samples, calculate the total composition (in %) of CrO_3 in each sample using:

$$CrO_3\ \%(w/w) = \frac{(A \times SA)(100\%) \times D \times GF}{(Sample\ wt)(1000\ \mu g/mg)}\ \text{(Bulk Samples)}$$

Where:
Sample wt = aliquot (in mg) of bulk taken in Section 6.4.3

7.5 Report air sample results (from base extractions) to the industrial hygienist as mg/m³ CrO_3.

7.6 For spray paint samples, also report results obtained from the digestion of the residue. Report each result from digested samples as mg/m³ chromium metal and insoluble salts. Each result can be combined with the result in Section 7.5 by the industrial hygienist if the paint used during sampling does not contain other chromium compounds. Before combining results, the industrial hygienist has to perform the following calculation:

CrO_3(residual) mg/m^3 = Cr metal (mg/m^3) x 1.923

Then:

Total CrO_3 mg/m^3 = CrO_3(residual) + CrO_3(extraction)

7.7 Report bulk sample results to the industrial hygienist as approximate per cent CrO_3.

8. References

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8.17. **Beyerman, K.:** The Analytical Behavior of Minutest Chromium Quantities, Part II. Z. Anal. Chem. 190: 346-369 (1962).

Polarogram of a 1 µg/mL Cr(VI) Standard

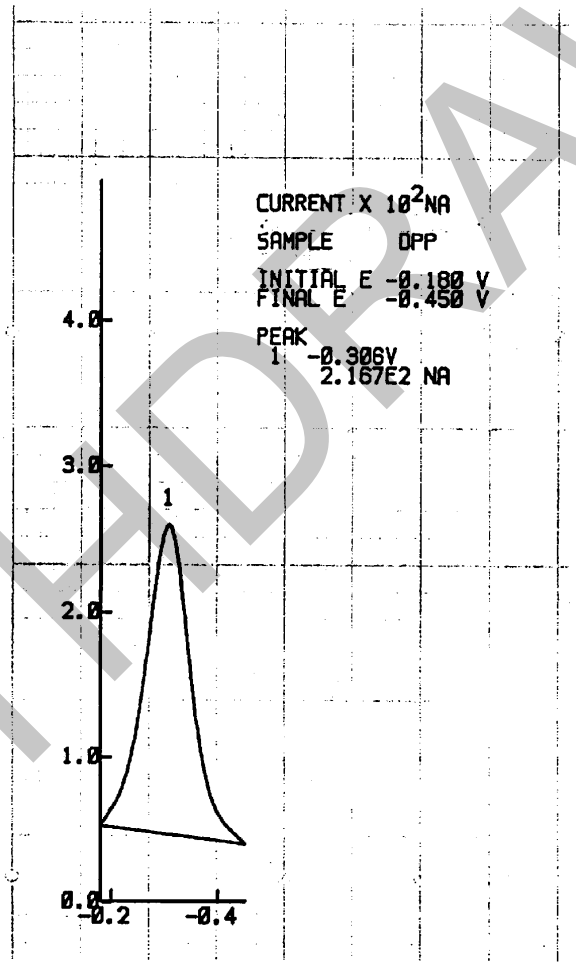

Figure 1

NA = nanoamperes

Hexavalent Chromium

OSHA Method ID-103 Backup (Revised June 1991)

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Introduction

The general procedure for collection and analysis of air samples of Cr(VI) is described in OSHA method no. ID-103 (11.1.). Briefly, the Cr(VI) sample is collected on a 37-mm polyvinyl chloride (PVC) filter and submitted to the laboratory for analysis. Any Cr(VI) on the filter is extracted with a hot sodium carbonate (Na_2CO_3) / sodium bicarbonate ($NaHCO_3$) buffer solution. The extract is then analyzed for Cr(VI) by differential pulse polarography (DPP) using a dropping mercury electrode. The analytical method has been validated using soluble and insoluble chromate compounds and a selected time weighted average (TWA) concentration range of about 0.005 to 0.01 mg/m^3 as Cr(VI) or 0.009 to 0.02 mg/m^3 as CrO_3 (840-L air sample). The TWA concentration selected for evaluation was considered a very low level at the time of the evaluation. When this method was first developed, the OSHA TWA permissible exposure limit (PEL) was 0.1 mg/m^3 as CrO_3 (11.2.). The PEL at the time of this revision is 0.1 mg/m^3 as a ceiling determination.

1. Evaluation Protocol

Unless mentioned otherwise, PVC filters obtained from Mine Safety Appliances (37-mm diameter, 5-µm pore size, model FWS-B, part no. 625413, Pittsburgh, PA) were used for all sample filter preparations. All filter samples were prepared and analyzed according to procedures described in the method (11.1.).

The experiments performed were:

1. Buffer/Extraction/Electrolyte (BEE) solution
2. Analysis - Desorption Efficiency
3. Analytical precision and accuracy
4. Interferences
5. Detection limits
6. Method comparison
7. Extraction efficiency
8. Mixed-cellulose ester filters

All samples were analyzed using a model 384 Polarographic Analyzer [Princeton Applied Research (PAR), Princeton, NJ) with the exception of the interference experiment. A model 374 Analyzer with a model 316 cell sequencer was used for this experiment.

All results were statistically examined using OSHA Inorganic Methods Evaluation Statistical Protocol (11.3.).

2. Buffer/Extraction/Electrolyte (BEE) Solution

It has been reported (11.4.) that the recovery of insoluble lead chromate in the presence of reducing agents such as magnetite (Fe_3O_4) is largely dependent on solution pH. At a low pH, less than 1% Cr(VI) was recovered; even at neutral pH, at least 10% of the Cr(VI) appeared to be reduced to Cr(III).

Acceptable recoveries of the Cr(VI) species occurred when a 7% Na_2CO_3 extraction solution was used. The most useful analytical pH range for Cr(VI) appeared to be between 10 and 11.

For the evaluation of OSHA method no. ID-103, a pH in this range was achieved by using a 10% Na_2CO_3 / 2% $NaHCO_3$ buffer solution. although a 7% Na_2CO_3 solution was used in the original study (11.4.), the BEE solution was thought to offer greater stability and solubility for the more insoluble chromate compounds. The BEE solution should satisfactorily prevent reduction to Cr(III) [or potential oxidation of any Cr(III) to Cr(IV)]. This 10% / 2% buffer was used as an extracting as well as a supporting electrolyte solution for all of the experiments in this backup report.

3. Analysis - Desorption Efficiency Study

Procedure: An analysis of a total of 18 spiked samples (6 samples at each of three test levels) was performed for each of four different chromate compounds. The compound used for spiking were lead, zinc, potassium, and calcium chromates. The spiked concentrations corresponded to about 0.0048, 0.009, and 0.019 mg/m^3 of CrO_3 when using an 840-L air sample volume. The step-by-step procedure used is listed:

3.1. Preparation of Stock Solutions

Each chromate compound was weighed on PVC filters, transferred to a 125-mL Phillips beaker, and the appropriate volume of BEE solution was added. The beakers were slowly heated with occasional swirling for 30 min. The solutions were cooled and then quantitatively transferred with deionized water (DI H_2O) rinses to individual volumetric flasks. The final amount of chromate in each solution was:

Stock Solution	Concn (µg/mL) as Cr(VI)
Lead chromate ($PbCrO_4$)	13.68
Zinc Chromate ($4ZnO\cdot CrO_3.3H_2O$)	24.68
Potassium Chromate (K_2CrO_4)	252.5
Calcium Chromate ($CaCrO_4$)	179.05

3.2. Preparation of Known Spiked Samples

Three sets of six spiked samples were prepared for each chromate compound studied by spiking appropriate volumes of stock solutions onto PVC filters. The filters were then placed into 125-mL Phillips beakers, 10 mL of BEE solution added, and the samples were heated and prepared as mentioned in the method (11.1.).

3.3. Analytical Procedure

Standards were prepared from 0.1 to 1 µg/mL Cr(IV). Samples and standards were analyzed according to Ref. 11.1.

Results: The analytical recoveries for the chromate compounds are presented in Tables 1 to 4. Recoveries and precision were excellent for all four compounds tested.

4. **Analytical Precision and Accuracy**

The analytical precision and accuracy data for results in Tables 1 through 4 are presented below. The pooled coefficients of variation (CV1) and the average analytical method recovery (AMR) over all test levels for individual chromate compounds are:

Compound	AMR	CV1(Pooled)
$PbCrO_4$	1.003	0.012
$4ZnO\cdot CrO_3.3H_2O$	1.053	0.017
K_2CrO_4	1.012	0.019
$CaCrO_4$	1.019	0.015

5. **Interferences**

Procedure: An experiment to test the potential interference from various amounts of Cr(III) and magnetite (Fe_3O_4) in the BEE solution was conducted. These reducing substances may coexist with Cr(VI) compounds in some workplace atmospheres and may also interfere with the analysis of Cr(VI) (11.4.). Differing amounts of Cr(VI), Cr(III), and Fe_3O_4 were spiked onto PVC filters. The concentrations of the spikes varied from 0 to 50 times the Cr(VI) concentration. Potassium chromate and chromium chloride ($CrCl_3$) solutions were used for the Cr(VI) and Cr(III) spikes, respectively. As shown in Table 5, eleven different mixture combinations and six samples of each combination were prepared and analyzed.

Results: The recoveries for Cr(VI) in solution with varied amounts of Cr(III) or Fe_3O_4 are shown in Table 5. The recovery range is between 97 and 103%. For the DPP method, there appears to be no significant effect on recovery even when Cr(III) and Fe_3O_4 are present in excess together as much as 10 and 50 times, respectively, over Cr(VI).

6. **Detection Limits**

Procedure: The qualitative and quantitative analytical detection limits of the method were determined by preparing BEE solutions containing varied amounts of K_2CrO_4 and then analyzing by DPP. The Rank Sum Test (11.5.) was used to determine the qualitative detection limit for Cr(VI). Blank samples and standards were analyzed and the results were ranked from lowest to highest signals. The standard concentrations ranged from 0.01 to 0.04 µg/mL as Cr(VI). The quantitative limit was determined by examining the recoveries and coefficients of variation of five sets of six standards. The concentration of these standards ranged from 0.02 to 0.1 µg/mL as Cr(VI).

Results: The results of the Rank Sum Test are shown in Table 6. As shown, the qualitative detection limit is 0.19 µg as CrO_3 (10-mL sample volume) and was determined at the 99% confidence level. Table 7 shows recoveries and CVs for the five sets of low concentration standards. Using conservative limits of:

$$CV < 10\%$$

$$\text{recovery} < \pm 10\% \text{ from theoretical}$$

the quantitative detection limit is 0.58 µg as CrO_3 (10-mL sample volume). The next standard below this concentration (0.038 µg/mL as CrO_3) displayed a recovery of 113.3% which is >10% of the true value.

7. **Method Comparison**

Procedure: A comparison of this polarographic analytical method with another method was conducted. The NIOSH colorimetric method (S317) for chromate (11.6.) was modified to allow use of the base extraction during sample preparation instead of the 0.5 N sulfuric acid (H_2SO_4) extraction. Samples were prepared by spiking PVC filters with solutions of $PbCrO_4$. The samples were extracted

and an aliquot was analyzed according to the method (11.1.). Another aliquot was acidified with 6 N H_2SO_4 and analyzed by the following procedure:

7.1 A total BEE sample solution volume of 10 mL was slowly and carefully acidified with 5 mL of 6 N H_2SO_4. After liberation of CO_2, each sample was diluted to a 25-mL volume with DI H_2O.

7.2 A 15 mL aliquot of the sample was taken, 0.5 mL of s-diphenylcarbazide (DPC) was added, and then analyzed colorimetrically at 540 nm as described in reference 11.6.

Results: The sample comparison data of the two methods at about 0.5, 1, and 2 times the selected TWA concentration are shown in Table 8. This data indicates the modified NIOSH colorimetric/DPC method and the DPP method will give similar results over the concentration range tested.

8. **Extraction Efficiency**

Procedure: An extraction efficiency study of Cr(VI) on PVC filters was conducted by spiking solutions of K_2CrO_4 onto FWS-B filters. These spikes were allowed to dry overnight, extracted, and then analyzed by polarography. Spikes were made with approximately 3.3, 4.9, and 9.8 µg as Cr(VI).

Results: The results of the extraction efficiency study are presented in Table 9. The average recovery over the three concentrations tested was 100.9%.

9. **Mixed-Cellulose Ester (MCE) Filters**

Procedure: A study of the stability of Cr(VI) on a MCE filter (type HA, 24-mm diameter, 0.45-µm pore size, cat. no. HAWP-024-00, Millipore Corp., Bedford, MA) was conducted. The reduction of Cr(VI) to Cr(III) on this type of media has been mentioned in the literature (11.4., 11.6.). To assess if the amount of Cr(III) would have any effect on Cr(VI) stability, differing amounts of Cr(III) were also added to the MCE filters.

Five different mixture combinations of Cr(VI) and Cr(III) were prepared from K_2CrO_4 and $CrCl_3$ solutions. Six samples of each mixture combination were prepared by spiking these solutions on MCE filters. These samples were extracted and analyzed according to Ref. 11.1.

Results: The results are reported in Table 10. A decrease of 20 to 40% in recovery was noted with the larger decrease occurring when no Cr(III) was present.

10. **Additional Information and Conclusions**

10.1 The collection efficiency of PVC filters for chromic acid was reported to be 0.945 ±0.035. The experiment was performed at a generated chromic acid concentration of 0.192 mg/m^3 (11.7.).

10.2 The molecular formula for the zinc chromate compound used in Section 3.1. was preliminarily determined by atomic absorption and then confirmed by X-ray diffraction analysis.

10.3 Analysis of other metals extracted into the BEE solution: Many metals, if extracted, can be analyzed by DPP. The peak potentials of lead and zinc salts in the BEE solution were experimentally determined to be -0.628 and -1.354 V, respectively. Since the peak is dependent on analytical conditions, these potentials may be slightly different with different instruments.

10.4 An additional evaluation of storage stability was recently conducted to determine if Cr(VI) is stable on PVC filters manufactured by Omega Specialty Instrument Co., Chelmsford, MA (cat. no. P-503700, 5-µm pore size, 37-mm diameter). Six filters were spiked with solutions of potassium dichromate. Three filters were analyzed by polarography after 1 week and three after 1 month of storage. The filters were stored in petri dishes and placed in a laboratory drawer. Recoveries were approximately 100%, indicating no significant storage problems for this PVC product.

10.5 Conclusions

This analytical method has been shown to be precise and accurate when analyzing four different chromate compounds commonly found in the workplace. Detection limit experiments indicated reasonable recoveries at concentration levels near 0.06 µg/mL as CrO_3. This is adequate for ceiling or TWA occupational exposure determinations; however, at least 15-min air samples should be taken for ceiling determinations since the detection limit may not be achievable for all polarographic instruments (0.06 µg/mL CrO_3 would equal 0.02 mg/m^3 for a 30-L air volume). Results compared well to those obtained using a modified colorimetric/DPC method, which indicates the modified method could possibly be used to analyze samples if a polarograph is unavailable. Spiked quality control samples should be prepared with the specific chromate compound(s) and taken through this alternate procedure first to assure no loss of Cr(VI). The spiked samples should be prepared in a matrix closely matching the industrial process being sampled.

A gain or decrease in Cr(VI) recoveries [possibly due to oxidation of, or reduction to Cr(III)] was not noted in any of the experiments performed with the exception of the MCE filter study. Filters composed of MCE appear unacceptable for collecting Cr(VI).

11. **References**

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11.4 Thomsen, E. and R.M. Stern: A Simple Analytical Technique for the Determination of Hexavalent Chromium in Welding Fumes and Other Complex Matrices. Scand. J. of Work, Environ. and Health 5: 386-403 (1979).

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11.6 National Institute for Occupational Safety and Health: NIOSH Manual of Analytical Methods. 2nd ed., Vol. 3 (DHEW/NIOSH Pub. No. 77-157-C). Cincinnati, OH: National Institute for Occupational Safety and Health, 1977. pp. S317-1-S317-6.

11.7 National Institute for Occupational Safety and Health: Documentation of the NIOSH Validation Tests by D. Taylor, R. Kupel and J. Bryant (DHEW/NIOSH Pub. No. 77-185). Cincinnati, OH: National Institute for Occupational Safety and Health, 1977.

These tables are best viewed on tablets, notebooks, or desktop computer screens.

Table 1
Analysis - Cr(VI)Using $PbCrO_4$ Spikes

v

LEVEL*								
- - - - - 0.5 × TWA - - - - -			- - - - - - 1 × TWA - - - - -			- - - - - - 2 × TWA - - - - -		
µg Taken	µg Found	AMR	µg Taken	µg Found	AMR	µg Taken	µg Found	AMR**
2.188	2.239	1.023	4.376	4.285	0.979	8.752	8.685	0.992
2.188	2.238	1.023	4.376	4.315	0.986	8.752	8.901	1.017
2.188	2.247	1.027	4.376	4.371	0.999	8.752	8.745	0.999
2.188	2.227	1.018	4.376	4.315	0.986	8.752	8.831	1.009
2.188	2.205	1.008	4.376	4.319	0.987	8.752	8.851	1.011
2.188	2.145	0.980	4.376	4.315	0.986	8.752	8.820	1.008
N =		6			6			6
Mean		1.013			0.987			1.006
Std Dev		0.017			0.006			0.01
CV1		0.017			0.006			0.009

Results are as µg Cr(IV)

* Selected TWA concentration of 0.009 mg/m³ as CrO_3 (840-L air volume)
** AMR = Analytical Method Recovery

CV_1 POOLED = 0.012

The average AMR for all levels is 1.003

These tables are best viewed on tablets, notebooks, or desktop computer screens.

Table 2
Analysis - Cr(VI)Using $4ZnO \cdot CrO_3.3H_2O$ Spikes

LEVEL*								
----- 0.5 × TWA -----			------ 1 × TWA -----			------ 2 × TWA -----		
µg Taken	µg Found	AMR	µg Taken	µg Found	AMR	µg Taken	µg Found	AMR**
2.221	2.411	1.085	4.442	4.685	1.055	8.883	9.457	1.065
2.221	2.306	1.033	4.442	4.685	1.055	8.883	9.541	1.074
2.221	2.306	1.033	4.442	4.738	1.067	8.883	9.160	1.031
2.221	2.323	1.048	4.442	4.693	1.057	8.883	9.020	1.015
2.221	2.328	1.048	4.442	4.693	1.057	8.883	9.193	1.035
2.221	2.328	1.048	4.442	4.748	1.069	8.883	9.477	1.067
N =		6			6			6
Mean		1.051			1.060			1.048
Std Dev		1.018			0.006			0.02
CV1		0.017			0.006			0.023

Results are as µg Cr(IV)

* Selected TWA concentration of 0.009 mg/m³ as CrO_3 (840-L air volume)
** AMR = Analytical Method Recovery

CV_1 POOLED = 0.017

The average AMR for all levels is 1.053

These tables are best viewed on tablets, notebooks, or desktop computer screens.

Table 3
Analysis - Cr(VI)Using K_2CrO_4 Spikes

LEVEL*								
- - - - - 0.5 × TWA - - - - -			- - - - - - 1 × TWA - - - - -			- - - - - - 2 × TWA - - - - -		
µg Taken	µg Found	AMR	µg Taken	µg Found	AMR	µg Taken	µg Found	AMR**
2.020	1.987	0.934	4.040	4.017	0.994	8.080	8.091	1.001
2.020	1.981	0.931	4.040	4.137	1.024	8.080	8.193	1.014
2.020	2.051	1.015	4.040	4.066	1.006	8.080	7.987	0.938
2.020	2.067	1.023	4.040	4.000	0.990	8.080	8.382	1.037
2.020	2.059	1.019	4.040	4.066	1.006	8.080	8.453	1.046
2.020	2.045	1.012	4.040	4.098	1.014	8.080	8.461	1.047
N =		6			6			6
Mean		1.006			1.006			1.022
Std Dev		0.019			0.013			0.02
CV1		0.019			0.012			0.024

Results are as µg Cr(IV)

* Selected TWA concentration of 0.009 mg/m^3 as CrO_3 (840-L air volume)
** AMR = Analytical Method Recovery

CV_1 POOLED = 0.019

The average AMR for all levels is 1.012

These tables are best viewed on tablets, notebooks, or desktop computer screens.

Table 4
Analysis - Cr(VI)Using $CaCrO_4$ Spikes

LEVEL*								
- - - - - 0.5 × TWA - - - - -			- - - - - - 1 × TWA - - - - -			- - - - - - 2 × TWA - - - - -		
µg Taken	µg Found	AMR	µg Taken	µg Found	AMR	µg Taken	µg Found	AMR**
2.149	2.275	1.059	4.297	4.215	0.981	8.594	8.819	1.026
2.149	2.174	1.012	4.297	4.295	1.000	8.594	8.753	1.019
2.149	2.179	1.014	4.297	4.314	1.004	8.594	8.819	1.026
2.149	2.188	1.018	4.297	4.314	1.004	8.594	8.812	1.025
2.149	2.196	1.022	4.297	4.331	1.008	8.594	8.879	1.033
2.149	2.188	1.018	4.297	4.355	1.013	8.594	9.126	1.062
N =		6			6			6
Mean		1.024			1.002			1.032
Std Dev		0.017			0.011			0.02
CV1		0.017			0.011			0.015

Results are as µg Cr(IV)

* Selected TWA concentration of 0.009 mg/m^3 as CrO_3 (840-L air volume)
** AMR = Analytical Method Recovery

CV1 POOLED = 0.015

The average AMR for all levels is 1.019

These tables are best viewed on tablets, notebooks, or desktop computer screens.

Table 5
Interference Study Theoretical Amount of Cr(VI) = 1.63812 mg

MIXTURE Composition*	1	2	3	4	5	6
	1:0:0	1:0:2.95	1:0:16.03	1:0:67.75	1:0.68:0	1:1.84:0
mg found as Cr(IV)	1.63667	1.68499	1.62845	1.57592	1.66940	1.67167
	1.60167	1.70349	1.62005	1.60476	1.66520	1.66222
	1.61506	1.68704	1.63686	1.58828	1.62625	1.75870
	1.62226	1.70349	1.64946	1.58211	1.68199	1.67167
	1.64696	1.64593	1.62110	1.59137	1.67989	1.61181
	1.61814	1.64593	1.67255	1.54501	1.65261	1.66642
N	6	6	6	6	6	6
Mean	1.62346	1.67848	1.63808	1.58124	1.66257	1.67375
Std Dev	0.01614	0.02640	0.02013	0.02023	0.02070	0.04743
CV1	0.010	0.016	0.012	0.013	0.012	0.028
Recovery (%)	99.1	102.5	100.0	96.5	101.5	102.2

MIXTURE Composition*	7	8	9	10	11
	1:8.07:0	1:0.93:1.99	1:2.09:5.45	1:4.95:13.69	1:9.14:52.14
	1.64322	1.67675	1.65995	1.59693	1.62005
	1.63059	1.65576	1.64316	1.62215	1.60009
	1.63165	1.69983	1.67150	1.63686	1.56539
	1.65059	1.67255	1.68619	1.57065	1.56749
	1.63586	1.69458	1.68514	1.62215	1.70715
	1.66952	1.70506	1.62005	1.61480	1.62005
N	6	6	6	6	6
Mean	1.64357	1.68409	1.66100	1.61059	1.61337
Std Dev	0.01478	0.01891	0.02578	0.02348	0.05190
CV1	0.009	0.011	0.016	0.015	0.032
Recovery (%)	100.3	102.8	101.4	98.3	98.5

* Composition = Ratio of Cr(VI): Cr(III): Fe_3O_4

These tables are best viewed on tablets, notebooks, or desktop computer screens.

Table 6
Qualitative Detection Limit Rank Sum Test

For Nstd = Nblank = 6

	Standard [as Cr(VI)]			
Rank	0.010 µg/mL	0.020 µg/mL	0.030 µg/mL	0.040 µg/mL
1	0 RBl	0 RBl	0 RBl	0 RBl
2	0 RBl	0 RBl	0 RBl	0 RBl
3	0 RBl	0 RBl	0 RBl	0 RBl
4	0 RBl	0 RBl	0 RBl	0 RBl
5	0 RBl	0 RBl	0 RBl	0 RBl
6	0 RBl	0 RBl	0 RBl	0 RBl
7	1.60 Std.	3.22 Std.	5.07 Std.	6.79 Std.
8	1.65 Std.	3.30 Std.	5.10 Std.	6.84 Std.
9	1.75 Std.	3.34 Std.	5.14 Std.	6.96 Std.
10	1.75 Std.	3.44 Std.	5.15 Std.	6.99 Std.
11	1.80 Std.	3.47 Std.	5.20 Std.	7.17 Std.
12	1.80 Std.	3.66 Std.	5.57 Std.	7.18 Std.
Rb =	21	21	21	21
C =	99.9%	99.9%	99.9%	99.9%

Where:

RBl = Reagent Blank signal (as nA × 102)

Std. = Standard signal (as nA × 102)

Rb = Sum of ranks for the Reagent Blank samples

C = Confidence level

As shown, the blank sample population gave significantly different signals than the standard population for all concentrations tested.

Qualitative detection limit = 0.010 µg/mL as Cr(VI) or 0.019 µg/mL as CrO_3

These tables are best viewed on tablets, notebooks, or desktop computer screens.

Table 7
Quantitative Detection Limit

Cr(VI) Level, µg/mL

	0.020 µg/mL		0.030 µg/mL		0.040 µg/mL		0.050 µg/mL		0.100 µg/mL	
No.	Found	AMR	Found	AMR	Found	AMR	Found	AMR	Found	AMR*
1	23.3	1.165	32.4	1.080	44.0	1.100	55.9	1.118	109.4	1.094
2	22.6	1.110	32.8	1.093	42.5	1.063	51.7	1.034	107.4	1.074
3	21.6	1.080	34.9	1.163	43.2	1.080	53.3	1.066	108.1	1.081
4	22.6	1.130	32.9	1.097	41.9	1.048	53.5	1.070	107.5	1.075
5	22.2	1.110	32.3	1.077	42.6	1.065	52.0	1.040	108.4	1.084
6	24.1	1.205	32.7	1.090	43.7	1.093	52.9	1.058	106.2	1.062
N	6		6		6		6		6	
Mean	22.7	1.133	33.0	1.100	43.0	1.075	53.2	1.064	107.8	1.078
Std Dev	0.87	0.045	0.96	0.032	0.020	0.020	1.49	0.030	1.08	0.011
CV1	0.039	0.039	0.029	0.029	0.018	0.018	0.028	0.028	0.010	0.010

* AMR = Analytical Method Recovery

Quantitative detection limit = 0.03 µg/mL as Cr(VI) or 0.058 µg/mL as CrO_3

These tables are best viewed on tablets, notebooks, or desktop computer screens.

Table 8
Comparison Study

Modified Diphenylcarbazide Method vs. Differential Pulse Polarography
Selected TWA Test Level = 0.009 mg/m^3 as CrO_3

Test Level	µg Taken	µg Found (DPC)	AMR (DPC)	µg Found (DPP)	AMR (DPP)
0.5 × TWA	2.188	2.162	0.988	2.239	1.023
	2.188	2.109	0.964	2.238	1.023
	2.188	2.141	0.979	2.247	1.027
	2.188	2.035	0.930	2.227	1.018
	2.188	2.120	0.969	2.205	1.008
	2.188	1.982	0.906	2.145	0.980
N		6		6	
Mean		2.092	0.956	2.217	1.013
Std Dev		0.069	0.032	0.038	0.018
CV1		0.033		0.017	
1 × TWA	4.376	4.412	1.008	4.285	0.979
	4.376	4.322	0.988	4.315	0.986
	4.376	4.479	1.024	4.371	0.999
	4.376	4.434	1.013	4.315	0.986
	4.376	4.288	0.980	4.319	1.003
	4.376	4.389	1.003	4.315	0.986
N		6		6	
Mean		4.387	1.003	4.332	0.990
Std Dev		0.071	0.016	0.040	0.009
CV1		0.016		0.009	
2 × TWA	8.752	9.044	1.033	8.685	0.992
	8.752	8.928	1.020	8.901	1.017
	8.752	8.953	1.023	8.745	0.999
	8.752	8.799	1.005	8.831	1.009
	8.752	8.657	0.989	8.851	1.011
	8.752	8.786	1.004	8.820	1.008
N		6		6	
Mean		8.861	1.012	8.806	1.006
Std Dev		0.140	0.016	0.078	0.009
CV1		0.016		0.009	

Results are reported as µg Cr(VI)

DPC = Colorimetric/DPC method (modified NIOSH S317 - used base extraction)
DPP = Differential Pulse Polarography (OSHA ID-103)

The average AMR for all levels using the DPC method is 0.990; for DPP 1.003

These tables are best viewed on tablets, notebooks, or desktop computer screens.

Table 9
Filter Extraction Efficiency - 37-mm PVC filter

µg Taken	µg Found	E.E.	µg Taken	µg Found	E.E.	µg Taken	µg Found	E.E.
						9.829	10.814	1.100
			4.914	5.379	1.095	9.829	10.601	1.079
3.276	2.899	0.885	4.914	5.195	1.057	9.829	10.412	1.059
3.276	2.919	0.891	4.914	5.320	1.083	9.829	10.412	1.059
3.276	2.784	0.850	4.914	5.169	1.052	9.829	10.751	1.094
3.276	2.623	0.801	4.914	5.234	1.065	9.829	10.519	1.070
3.276	3.094	0.944	4.914	5.392	1.097	9.829	10.425	1.061
3.276	2.832	0.864	4.914	5.425	1.104	9.829	10.707	1.089
						9.829	10.580	1.076
N		6			7			9
Mean		0.873			1.079			1.076
Std Dev		0.048			0.021			0.015
CV1		0.054			0.019			0.014

Results are listed as µg Cr(VI)

E.E. = Extraction Efficiency

* Selected TWA = 0.009 mg/m^3 as CrO_3

These tables are best viewed on tablets, notebooks, or desktop computer screens.

Table 10
Mixed-Cellulose Ester Filters For Cr(VI) Analysis

Theoretical Amount Spiked On Each Filter = 2.2262 mg as Cr(VI)

Mixture No.	1*	2	3	4	5
Composition**	1:0	1:2.31	1:6.02	1:12.24	1:0
mg Cr(VI) found	2.2863	1.7808	1.8280	1.7835	1.3765
	2.3188	1.6878	1.8365	1.7722	1.3810
	2.3152	1.8595	1.8203	1.6882	1.3783
	2.2943	1.7949	1.8304	1.7345	1.3946
	2.3105	1.7949	1.8203	1.6845	1.3935
	2.2871	1.7997	1.8203	1.7141	1.3898
N	6	6	6	6	6
Mean (mg)	2.3020	1.7863	1.8260	1.7295	1.3857
Std Dev (mg)	0.0145	0.0555	0.0068	0.0418	0.0080
CV1	0.006	0.031	0.004	0.024	0.006
Recovery (%)	103.4	80.2	82.0	77.7	62.2

* Mixture No. 1 consisted of six samples only spiked with Cr(VI). Mixed-cellulose filters and Cr(III) spikes were not added to these six solutions. All other samples contained mixed-cellulose ester filters.

** Composition = Ratio of Cr(VI): Cr(III)