

**Other Test Method 35 –  
Measurement of Particulate Matter and Other Heavy Metal Emissions from Electric Arc  
Welding Processes**

This method was developed to quantify emissions of particulate matter (PM) and heavy metals from electric arc welding processes in order to create emissions factors. Welding fumes from different process/electrode combinations are captured inside a conical weld fume chamber and collected on an appropriate analytical fiber filter installed at the exit to this chamber. The filters are submitted to a laboratory for analysis of Cr(VI), total Cr, Mn, Pb, Ni and mass of total fume. The analytical results can then be used to calculate emission factors for each component. More specifically, the emissions produced from electric arc welding processes are collected in accordance with the American Welding Society (AWS) F1.2:2006, *Laboratory Method for Measuring Fume Generation and Total Fume Emission of Welding and Allied Processes (AWS F1:2)* and analyzed in accordance with analytical methods developed by the National Institute for Occupational Safety and Health (NIOSH), and the Occupational Safety and Health Administration (OSHA) to determine the total concentrations of Hexavalent Chromium (Cr(VI)) and total Chromium (Cr), Nickel (Ni), Lead (Pb) and Manganese (Mn). The resulting analytical data, along with the process data collected during the testing (amount of electrode consumed), may then be used to calculate emission factors for the electrode in terms of mass of pollutant per mass of electrode consumed.

This method was developed and submitted by the National Shipbuilding Research Program (NSRP) Environmental Panel to EPA's Office of Air Quality, Planning and Standards – Air Quality Assessment Division – Measurement Technology Group (MTG) for inclusion into the Other Test Method (OTM) category on EPA's Emission Monitoring Center (EMC) website at <http://www.epa.gov/ttn/emc/>. The NSRP Environmental Panel worked with Concurrent Technologies Corporation (CTC) as a primary contractor with subcontractors Applied Research Laboratory at the Pennsylvania State University (ARL-PSU) and SoftTek Systems, Inc. as consultants and DataChem Laboratories, Inc. as the analytical laboratory.

As a reminder, the posting of a test method on the OTM portion of the EMC is neither an endorsement by EPA regarding the validity of the test method nor a regulatory approval of the test method. The purpose of the OTM portion of the EMC is to promote discussion of developing emission measurement methodologies and to provide regulatory agencies, the regulated community, and the public at large with potentially helpful tools.

We would advise that any further investigation of this method include confirmation that significant sample does not remain on the walls of the chamber following each welding test run. A discussion of this issue can be found in the document attached to the method as Appendix F. The reader is encouraged to review this appendix for additional information.

**OTHER TEST METHOD 35 -  
MEASUREMENT OF PARTICULATE  
MATTER AND HEAVY METAL EMISSIONS  
FROM ELECTRIC ARC WELDING  
PROCESSES**

**Draft**

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## LIST OF ACRONYMS AND ABBREVIATIONS

AES	Atomic Emission Spectrophotometry
ARL	Applied Research Laboratory
AWS	American Welding Society
CARB	California Air Resources Board
CFM	Cubic Feet per Minute
CFR	Code of Federal Regulations
Cr	Chromium
Cr(III)	Trivalent Chromium
Cr(VI)	Hexavalent Chromium
CTC	Concurrent Technologies Corporation
DPM	Diesel particulate matter
EFs	emissions factors
EH&S	Environmental, Health and Safety
EPA	Environmental Protection Agency
ETF	Environmental Technology Facility
FCAW	Flux Cored Arc Welding
GMAW	Gas Metal Arc Welding
HAP	Hazardous Air Pollutants
ICP	Inductively Coupled Plasma
JSA	Job Safety Analyses
Mn	Manganese
MSDS	Material Safety Data Sheet
Na <sub>2</sub> CO <sub>3</sub>	10% sodium carbonate
NaHCO <sub>3</sub>	2% sodium bicarbonate
NELAP	National Environmental Laboratory Accreditation Program
NESHAP	National Emissions Standards for Hazardous Air Pollutants
Ni	Nickel
NIOSH	National Institute for Occupational Safety and Health
NMAM	NIOSH Manual of Analytical Methods
NSRP	National Shipbuilding Research Program
OSHA	Occupational Safety and Health Administration
Pb	Lead
PSU	Pennsylvania State University
PTR	Program Technical Representative
PVC	Polyvinyl Chloride
QA	Quality Assurance
QC	Quality Control
RSD	Relative Standard Deviation
SAP	Sampling and Analysis Plan

## **LIST OF ACRONYMS AND ABBREVIATIONS**

SMAW	Shielded Metal Arch Welding
SOP	Standard Operating Procedures
UV	Ultraviolet

## **1.0 SCOPE AND APPLICATION**

### **1.1 Purpose**

This testing method can be used to collect emissions data from electric arc welding processes to create emissions factors that accurately represent those processes.

This document details the experimental materials, equipment, procedures, analytical methods, and controls that are used to collect the weld fume emissions data.

### **1.2 Objectives**

The primary objectives of this program are the following:

1. Collect the emissions produced from electric arc welding processes in accordance with the American Welding Society (AWS) F1.2:2006, *Laboratory Method for Measuring Fume Generation and Total Fume Emission of Welding and Allied Processes (AWS F1.2)*.
2. Analyze the emissions in accordance with analytical methods developed by the National Institute for Occupational Safety and Health (NIOSH), and the Occupational Safety and Health Administration (OSHA) to determine the total concentrations of Hexavalent Chromium (Cr(VI)) and total Chromium (Cr), Nickel (Ni), Lead (Pb) and Manganese (Mn).
3. Use the resulting analytical data, along with the process data collected during the testing (amount of electrode consumed), to calculate emission factors for the electrode in terms of mass of pollutant per mass of electrode consumed.

### **1.3 Developing Organization**

This method was developed by the National Shipbuilding Research Program (NSRP) Environmental Panel with Concurrent Technologies Corporation (CTC) acting as the primary contractor. CTC subcontracted Applied Research Laboratory at the Pennsylvania State University (ARL-PSU) and SoftTek Systems, Inc. as consultants for the project and DataChem Laboratories, Inc. as the analytical laboratory.

## **2.0 SUMMARY OF METHOD**

The intent of this method is to determine scientifically valid emissions factors for electric arc welding processes. Welding fumes from different process/electrode combinations can be collected on appropriate analytical fiber filters. The filters can then be submitted to an industrial hygiene testing laboratory for the analysis of Cr(VI), Cr, Mn, Pb, Ni and mass of total fume. The analytical results can then be used to calculate EFs for each of these components.

## **3.0 DEFINITIONS**

### **3.1 Arc Welding Processes**

Electric arc welding, the most frequently used process, includes many different variations that involve various types of electrodes, fluxes, shielding gases, and types of equipment. Electric arc welding can be divided into processes using nonconsumable electrodes and consumable electrodes. In electric arc welding, a flow of electricity across the gap from the tip of the welding electrode to the base metal creates the heat needed for melting and joining the metal parts. The electric current melts both the electrode and the base metal at the joint to form a molten pool, which solidifies upon cooling (*AP-42*). A description of two common electric arc welding processes for which this method was designed for and has been applied is provided below. This method could potentially be used to generate emissions data from other welding and/or cutting processes, with proper modification.

#### **3.1.1 Shielded Metal Arc Welding (SMAW)**

SMAW utilizes heat produced by an electric arc to melt a covered electrode and the welding joint at the base metal. During operation, the rod core both conducts electric current to produce the arc and provides filler metal for the joint. The core of this covered electrode consists of either a solid metal rod of drawn or cast material or a solid metal rod fabricated by encasing metal powders in a metallic sheath. The electrode covering provides stability to the arc and protects the molten metal by creating shielding gases by vaporization of the cover (*AP-42*).

#### **3.1.2 Flux Cored Arc Welding (FCAW)**

FCAW is a consumable electrode welding process that uses the heat generated by an arc between the continuous filler metal electrode and the weld pool to bond the metals. This flux cored electrode consists of a metal sheath surrounding a core of various powdered materials. During the welding process, the electrode core material produces a slag cover on the face of the weld bead. The welding pool can be protected from the atmosphere either by self-shielded vaporization of the flux core or with a separately supplied shielding gas (*AP-42*).

#### **3.1.3 Gas Metal Arc Welding**

Gas metal arc welding (GMAW) is a consumable electrode welding process that produces an arc between the weld pool and a continuously supplied filler metal. An externally supplied gas is used to shield the arc. GMAW originally was referred to as metal inert gas (MIG) welding because it used an inert gas for shielding. Although it still is sometimes called MIG welding, developments have led to the use of both inert and reactive gases. A variation of the GMAW process, referred to as metal cored electrodes, uses a tubular electrode filled mostly with metallic powders forms. These types of electrodes must use a gas shield to prevent contamination of the molten weld by the atmosphere. The American Welding Society (AWS) considers metal cored electrodes a part of GMAW, although metal cored electrodes are grouped with flux cored electrodes



by foreign welding associations. Advantages of GMAW include its ability to be operated in semiautomatic, machine, or automatic modes. It is the only consumable process that can weld all commercially important metals, such as carbon steel, high-strength low alloy steel, stainless steel, nickel alloys, titanium, aluminum, and copper. A weld can be performed in all positions with the proper choice of electrode, shielding gas, and welding variables. Compared with shielded metal arc welding (SMAW), the deposition rates and welding rates are higher for GMAW. Also, the continuous electrode feed makes long welds possible without stops and starts. On the downside, the equipment for GMAW is more complex, more expensive, and less portable than the SMAW process.

## **3.2 Filter Media**

### **3.2.1 Tissuquartz™ Filter, Quartz, No Support Pad, 8" x 10"**

- Autoclavable, binder-free, heat-treated to remove trace organic impurities, high-purity microfibers for collecting diesel particulates and trace-level environmental pollutants.
- Superior purity for collection of elemental/organic carbon, Diesel Particulate Matter (DPM), and trace-level contaminants.
  - Heat-treated to reduce trace organics
  - Low-metal background
  - Binder-free
  - High flow rate and filtration efficiency
  - Withstand temperature up to 1832° F (1000°C)
- Specified in NIOSH method 5040 for Elemental Carbon (Diesel Particulates (*SKC Website (1)*)).

### **3.2.2 Type AE Glass, Glass Fiber, No Support Pad, 1.0 µm, 8" x 10"**

- High-temperature tolerant
- Liquid nominal pore size of 1.0 µm
- High-particle retention (*SKC Website(2)*)

## **4.0 INTERFERENCES**

### **4.1 OSHA ID-215 Hexavalent Chromium**

The OSHA ID-215 uses alkaline extraction condition which prevents the reduction of Cr(VI) to Cr(III) and includes the addition of phosphate buffer/magnesium sulfate to the extraction media to reduce interferences from iron (II). Cr(VI) is then separated from any Cr(III) that is present in the sample using ion chromatography. Finally, post-column derivatization of the Cr(VI) with 1,5-diphenylcarbazide is performed to allow analysis using Ultraviolet-Visible (UV-Vis) detection at 540 nm. The combination of stabilization, separation and derivatization provides for a very specific analysis with a minimum of interference (OSHA ID-215).

## **4.2 NIOSH 7300 Elements by Inductively Coupled Plasma (ICP)**

The NIOSH 7300 method states that spectral interferences are the primary interferences encountered in Inductively Coupled Plasma Atomic Emission Spectrophotometry (ICP-AES) analysis. These are minimized by judicious wavelength selection, inter-element correction factors and background correction (*NIOSH 7300*).

## **5.0 SAFETY**

### **5.1 Welding Safety**

A qualified welder shall complete all welding activities associated with a testing event. The welder shall be properly trained and all activities shall be conducted in accordance with applicable OSHA regulations, including 29 Code of Federal Regulations (CFR) 1910 Subpart Q - Welding, Cutting, and Brazing.

All welding activities are completed inside the conical weld fume chamber. The fume chamber has a shield holder where shaded glass is placed to protect the welder from the flash of the welding arc. The appropriate shade level shall be placed in the holder before welding activities are initiated. OSHA Standard Number 1910.252, Welding, Cutting, and Brazing, should be referenced to determine the appropriate shade level for each welding activity. All other study participants are protected from the welders flash by the chamber.

The fume chamber system is designed to capture and contain all welding fumes, and it is anticipated that a minimum of 99.9% of the hazardous particulate constituents in the exhaust air will be captured on the filter. As an added safety precaution, it is recommended that a local exhaust ventilation system be placed at the chamber's blower outlet to capture and remove all exhaust air from the work environment.

### **5.2 Sample Collection Safety**

Participants involved in all sampling activities shall wear nitrile gloves and safety goggles when handling any filter media and/or preservation solutions. In addition, all participants should wear safety glasses and safety shoes during the testing event.

## **6.0 EQUIPMENT AND SUPPLIES**

### **6.1 Welding Test Chamber**

The specific chamber shall be constructed following the guidelines of AWS F1.2:2006, with the exception that the top of the chamber must be reduced to a diameter of 8" (rather than the specified 12") to allow the use of 8" high volume fiber filters with compositions

that are suitable for the analytical analysis via the approved OSHA and NIOSH methodologies. An example of a modified weld fume chamber is shown in Figure 1.



**Figure 1. NSRP Weld Fume Chamber**

The weld gun is inserted either through the front access port or through the side hand access port of the fume chamber.

A regenerative blower draws the weld fume that is generated up through the fume chamber exhaust duct at a flow of 709 to 989 Liters (L)/minute (25 to 35 Cubic Feet per Minute (CFM) ) as specified in Section 4.2.2 of the AWS F1.2:2006. The blower must be equipped with an adjustable frequency drive that controls the blower speed to maintain appropriate flow rates and pressure drops across the filter. The flow rate must be measured using an air flow meter and displayed on a gauge that is accessible during the testing event, preferably mounted on the control panel of the weld fume chamber.

A pressure drop gauge which reports the pressure drop across the filter in inches of water must also be included and visible during the testing event. This pressure drop gauge will indicate the amount to which the filter is loading. It is recommended that this also be mounted on the control panel of the weld fume chamber.

An example of a recommended control panel with gauges is shown in Figure 2. A detailed description of all recommended equipment installed on the weld fume chamber can be found in the Weld Fume Chamber Manual that is attached in Appendix A. The

AWS F1.2:2006 can be purchased from the AWS website, [www.aws.org](http://www.aws.org), and is recommended to support this method.



**Figure 2. Control Panel with Gauges**

The exhaust flow rate must be monitored to make sure that the flow through the chamber does not drop below the minimum 25 CFM specified in AWS F1.2:2006. The purpose of this requirement is to ensure that all fumes are drawn up through the filter where it is captured, and that none of the fume escapes through the access ports or at the bottom of the chamber. Reproducibility of the results, with a Relative Standard Deviation (RSD) of less than 20%, with a minimum of 3 data points from the mass of fume captured from a specific consumable, at specified welding parameters, will demonstrate that the system is in calibration. The mass of electrode consumed for each process/electrode combination must be calculated upon receipt of the gravimetric results from the lab to demonstrate consistent capture of fume on the filters. This data must be presented with testing results to verify the precision of welding fume generation and fume capture.

## **6.2 Filters**

The selection of filters for the capture of weld fume in the AWS weld fume chamber involves the consideration of a number of factors:

- Ability to filter fine fume particulates from the air,
- Capacity to handle high flow rates through the filter for use in the AWS chamber,
- Suitability for use in the selected OSHA and NIOSH methods for the analysis of heavy metals Cr, Mn, Pb, Ni and Cr(VI), and
- Available in sizes of at least 8" diameter.

AWS F1.2:2006 calls for the use of a pad of glass fiber insulation to filter the fume from the test chamber exhaust stream. The use of the glass fiber insulation pad allows for gravimetric analysis of the total mass of fume, but not for quantitative chemical analysis of individual metal components in the fume.

In addition, Chris Halm at the California Air Resources Board (CARB) reports that the AWS-recommended filter pad does not efficiently capture all fumes that are generated; at times over 10% of the fume mass passes through the glass fiber filter pad (*Halm*). Halm therefore recommends the use of Whatman Glass Microfiber filters, EPM-2000 for more complete capture of particulates.

Whatman Glass Microfiber EPM-2000 filter, Pall Tissuquartz™ quartz fiber filter, and Pall A/E glass fiber filter are all specifically designed for use with high volume air samplers (*VWR, Pall*). They capture greater than 99.9% of (Dispersed Oil Particulate.) DOP 0.3µm particulates and they are available in 8" x 10" sheets, which are large enough to capture the fumes from the cross-sectional area of the 8" diameter openings in the AWS fume chamber.

OSHA method ID-215 for Cr(VI) analysis calls for the use of Polyvinyl Chloride (PVC) or quartz filters. Because PVC membrane filters are not available in sizes larger than 4" diameter they are not suitable for this application. However, the Pall quartz membrane filters can be used, provided that they are inserted into a 2% sodium bicarbonate (NaHCO<sub>3</sub>)/10% sodium carbonate (Na<sub>2</sub>CO<sub>3</sub>) solution immediately after sampling in order to quench the conversion of Cr(VI) to Cr(III) on the filters.

NIOSH 7300 for heavy metals analysis allows for the use of glass fiber filters, making the 8" x 10" Pall A/E glass fiber filters acceptable for the Cr, Mn, Pb and Ni analysis. Thus, for the purposes of this method, and based on the discussion above, Pall Tissuquartz™ quartz fiber filters shall be used for all samples collected in the AWS weld fume chamber that will be tested for Cr(VI) by OSHA ID-215; and, Pall A/E glass fiber filters shall be used for all AWS weld fume chamber samples that will be tested for total metals by NIOSH 7300.

Prior to the testing events, the 8" x 10" filters must be cut to an 8" diameter, conditioned, pre-weighed and placed in a labeled storage bag/envelope. It is recommended that all pre-sampling activities be completed by the analytical testing laboratory that will analyze the samples.

It is recommended that these filters be stamped out using an 7 31/32" diameter cutting die, machined to have a sharp edge as presented in Figure 3.



**Figure 3. Die to Stamp Out**

It is recommended that the filters placed individually in labeled storage bags and envelopes (Figures 4 and 5), for shipment to the testing location.



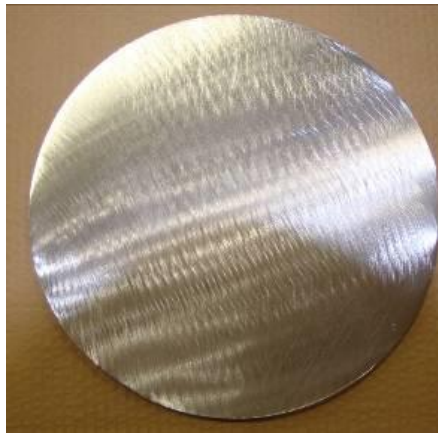
**Figure 4. Filter in Labeled Bag**



**Figure 5. Filter Envelopes**

### **6.3 Welding Materials**

The type of electrodes and base metals shall be selected based on the objectives of the testing event, and must reflect the actual process that the testing organizations wishes to represent with the emissions factors that are developed. The base metal shall be cut into 12" diameter plates for placement into the fume chamber as shown in Figure 6.



**Figure 6. 12" Diameter Plates for Placement into the Fume Chamber**

## **7.0 REAGENTS AND STANDARDS**

### **7.1 Sampling Reagents**

A 10% sodium carbonate ( $\text{Na}_2\text{CO}_3$ )/ 2% sodium bicarbonate  $\text{NaHCO}_3$  solution shall be used to quench the conversion of Cr(VI) to Cr(III) after sampling (*OSHA ID-215*).

### **7.2 Analytical Reagents**

Reagents and standards required by OSHA ID-215 and NIOSH 7300 analytical methodologies shall be used by the analytical laboratories. These methodologies can be found in Appendices B and C, respectively.

## **8.0 SAMPLE COLLECTION, PRESERVATION, STORAGE AND TRANSPORT**

Test Run Data Log sheets shall be used during testing to document welding times, fume chamber run times, sampling times, flow rate, pressure drop, volts and amps, along with the shielding gases and base metals used. All welding times, electrode weights, filter types and identification numbers, room temperature and humidity, and any special circumstances, problems or changes must be noted on the log sheets. A Test Run Data Log sheet used to support this method is provided in Appendix D.

It is recommended that all welding parameters be established based on what is recommended by the consumables suppliers, as referenced on their Technical Product Data Sheets, or based on what is commonly used within the industry that is subject to the testing. The source of the established test parameters must be documented along with a justification as to why those parameters were selected for use in the testing. The actual test parameters used must be recorded in the Test Run Data Log at the time of testing.

Welding with each of process/electrode combinations shall be conducted within a conical test chamber (Figures 7 and 8) meeting the requirements of the American Welding Society test method AWS F1.2:2006 (Appendix C). The specific chamber must be constructed following the guidelines of AWS F1.2:2006, with the exception that the top of the chamber reduced to a diameter of 8" (rather than the specified 12") to allow the use of 8" high volume fiber filters with compositions that are suitable for the analytical analysis via the approved OSHA and NIOSH methodologies.

All welding runs must be conducted within the weld fume chamber for selected welding process/electrode combination that is to be tested. The mass of electrode consumed in each run shall be measured and recorded, and the weld fumes shall be collected on 7 31/32" fiber filters, which shall be tested as follows.

The welding process and electrode under testing must be set up within the weld fume chamber. The weight of the electrode shall be recorded before and after each run to maintain a record of how much was consumed during each welding run. When using



stick electrodes (SMAW), an initial and final rod weight shall be recorded in the Test Run Data Log to determine the amount of electrode consumed. When using wire electrodes (FCAW and GMAW), the wire feed speed shall be determined (inches/15 minutes) and the wire mass per unit length measured (grams/inch) prior to welding. The welding time shall be recorded on the field data sheets. Using this information, the mass of weld wire consumed for each test run can be calculated. The type and size of the electrode, the base metal, and the volts and amps for the welding run must be recorded.

An appropriate filter shall be selected and assigned a field identification name and number that correspond to the welding process (FCAW, SMAW, or GMAW), electrode type (e.g., 309 or 7018) and the run number. Pall Tissuquartz™ quartz fiber filters shall be used for all samples collected in the AWS weld fume chamber that will be tested for Cr(VI) by OSHA ID-215 and Pall A/E glass fiber filters shall be used for all AWS weld fume chamber samples that will be tested for total metals by NIOSH 7300. The field identification name and number shall be recorded in the Test Run Data Log.

The filter must be removed from its labeled sampling container and placed on the bottom side of the gasketed sampling cage and clamped in place with a gasketed locking ring. The cage and filter is inserted into the top of the weld fume chamber. A gasketed top is put into place and clamped down. Figure 7 provides illustrations of the process recommended to install the filter into the weld fume cage and chamber.



**Figure 7. Placing Filter in Weld Fume Chamber**

After inserting the filter into the weld fume chamber, the welder shall position themselves for welding as demonstrated in Figure 8 below.



**Figure 8. Welding Inside Weld Fume Chamber**

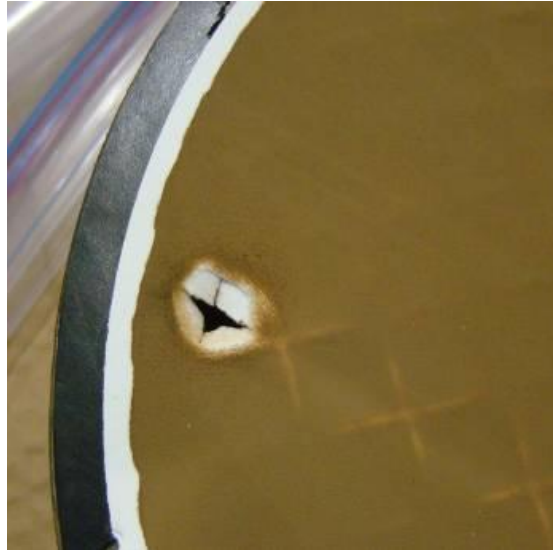
Once the welder is in position, the automated turntable inside the chamber and blower are started, and the starting flow rate in CFM and pressure drop in “inches of water” shall be recorded. The initial flow rate for each run with the blower at maximum capacity is expected to range from 38-43 CFM, and the pressure drop across the filter is expected to range from 17-27 inches of water with a clean filter (based on design specifications from weld fume chamber manual).

A timekeeper shall be utilized, and will signal the welder to start welding and start the timer when the arc is made between the electrode and base metal. As the filter loads with particulates from the fume, the flow rate will continually decrease and the pressure across the filter will continually increase to an expected range of 35–40 inches of water. Welding must be stopped before the flow rate drops below 25 CFM, which is the minimum specified in AWS F1.2:2006 to ensure that the fume does not escape the chamber. The rate of increase in pressure drop and decrease in flow rate will depend on the type of filter and the fume generation rate or filter loading rate. Filter loading will be dependent on the type of welding process, electrode, and process conditions. Welding times shall be regulated to between 7 and 25 seconds, depending on the welding process, to ensure that the flow rate does not drop below the required 25 CFM and the pressure does not become high enough to tear or damage the filter.

The blower shall be left operational for an additional 60 seconds after the welding is stopped in order to capture all weld fumes from the chamber, as specified in the AWS F1.2:2006.

After the welding run has been completed and the blower is allowed to run for an additional minute, the blower shall be turned off and the filter cage shall be removed from the chamber. At this point the filter must be inspected for any signs of fume loss. As part of this inspection, the filter must be examined to ensure that there were no punctures or tears in the filter (Figure 9), and that the outer ring of the filter is clean, indicating that there was a tight seal on the filter cage and that no fume had escaped

around the sides. Figure 10 demonstrates a filter that passed this inspection because a solid white ring is visible around the filter.

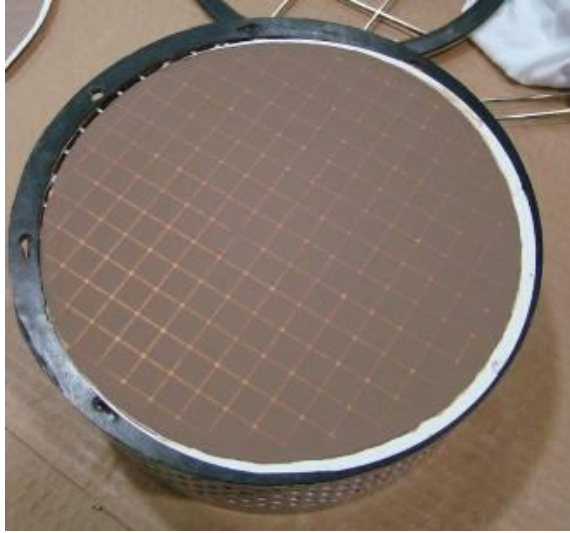


**Figure 9. Small Puncture Noted in a Filter Due to Increased Pressure**



**Figure 10. Filter That Would Pass Inspection Demonstrating No Fume Was Lost**

For comparison purposes, Figure 11 demonstrates a filter that did not pass this inspection.



**Figure 11. Filter that did not Pass Inspection Indicating Fume May Have Been Lost**

Any filters that do not pass inspection due to an incomplete seal and/or punctures in the filters must be discarded and the test re-run.

The quartz fiber filters (used for gravimetric analysis) and the glass fiber filters (used for gravimetric and metals analysis) shall be removed from the cage, folded into quarters, and inserted back into the labeled sample container and into an envelope (Figure 12).



**Figure 12. Removing Fume Sample from Weld Fume Chamber**

The quartz fiber filters that will be used for Cr(VI) analysis shall be folded into quarters and inserted into individual vials (Figure 13) containing 25 milliliters (ml) of a  $\text{Na}_2\text{CO}_3/\text{NaHCO}_3$  solution (*OSHA ID-215*).



**Figure 13. Vial of Sodium Bicarbonate Solution**

This  $\text{Na}_2\text{CO}_3/\text{NaHCO}_3$  solution will quench the conversion of Cr(VI) to Cr(III) on the filters (*OSHA ID-215* and *Chang et. al.*). The vials shall be stored in a freezer below the U.S. EPA recommended  $4^\circ\text{C}$  to further inhibit the conversion of Cr(VI). The samples shall be packed in dry ice for shipment to the laboratories.

The conical portion of the fume chamber must be removed, so that the inside can be blown out with an air hose and wiped clean before starting a new welding process/electrode combination (Figure 14).



**Figure 14. Cleaning the Chamber between runs**

## **9.0 QUALITY CONTROL**

### **9.1 Sampling Control Blanks**

#### Media Blanks

One (1) blank unused Tissuquartz fiber filter shall be folded and inserted into a vial containing 25 ml of the 10% Na<sub>2</sub>CO<sub>3</sub>/2% NaHCO<sub>3</sub> solution. This vial will be analyzed for Cr(VI) via the OSHA ID-215 method to determine if there is any Cr(VI) contamination in the filter material and/or the 10% Na<sub>2</sub>CO<sub>3</sub>/2% NaHCO<sub>3</sub> solution.

One (1) blank unused glass fiber filter shall be analyzed by NIOSH 7300 to determine if there is any background metal contaminant in the filter media.

#### Field Blanks

One (1) Tissuquartz fiber filter and one (1) glass fiber filter each shall be placed in the weld fume chamber during separate blank fume chamber runs (no welding). The blower is to be left run for a total of two (2) minutes without any welding activity. Both filters shall be analyzed gravimetrically via the NIOSH 0500 method. The glass fiber filter shall be analyzed via the NIOSH 7300 method to determine if there is any metal contaminant present in the fume chamber.

A separate Tissuquartz fiber filter shall be placed in the weld fume chamber during a blank fume chamber run. The blower shall be run for a total of two (2) minutes without any welding activity. This filter shall be folded and inserted into a vial containing the 25 mL 10% Na<sub>2</sub>CO<sub>3</sub>/2% NaHCO<sub>3</sub> solution. This vial shall be analyzed for Cr(VI) via the OSHA ID-215 method to determine if there is any Cr(VI) contamination in the chamber.

### **9.2 Sample Control**

All samples collected shall be assigned a unique sample identification number that clearly discerns it from other similar samples and provides information necessary to trace the sample to relevant field data sheets. Immediately after sample collection, each sample shall be placed in a suitable storage container and labeled with the unique sample identification number, the date and the initials of the person packaging the sample.

Complete laboratory chain-of-custody records shall be kept for each sample set, documenting all transfers in the possession of the samples, and documenting that the samples were in constant custody from collection to testing at the contracted analytical testing laboratory.

### **9.3 Records and Document Control**

The Test Run Data Logs are intended to provide sufficient experimental details, data, and observations to enable reconstruction of events that occurred during test and sampling activities. Additional data and observations may be included in a Field Data Notebook as

well. All entries in the Test Run Data Logs or in the Field Data Notebook shall be made with indelible ink and must be legible, accurate and complete. All entries shall include sample identification numbers, as necessary, to trace the samples collected to the recorded test information. If an error is made when recording test data, the method of correction is to draw a line through the error and enter the correct information. The erroneous information will not be obliterated. All corrections shall be initialed and dated. Test Run Data Logs shall be stored in a manner that protects them from loss or damage, and must become part of the project record file.

Completed copies of the chain-of-custody forms shall be retained in the project record file for traceability in case a sample is lost or destroyed.

#### **9.4 Analytical Laboratory QA/QC**

It is recommended that all samples are analyzed by an accredited (National Environmental Laboratory Accreditation Program (NELAP) or American Industrial Hygiene Association (AIHA)) testing laboratory, following established methods and protocols. Quality Assurance (QA) and Quality Control (QC) procedures cited within the specified OSHA and NIOSH methods shall be followed and reported.

#### **9.5 Data Review and Reporting**

All data collected during the testing event shall be entered into a Microsoft™ Excel spreadsheet and organized for calculation of emission factors. Data included in the spreadsheet shall be verified as accurate. Emission factors shall be calculated and reported in units consistent with those used by the U.S. EPA.

A hard copy of the data shall be included in the final testing summary report. An electronic version of the data shall become part of the project record file.

A final testing summary report shall be written. It must include photographs of the test setup; welding, sampling and testing details; copies of the raw data; sample calculations; Microsoft™ Excel files; and calculated emission factors.

### **10.0 CALIBRATION/STANDARDIZATION**

#### **10.1 Fume Chamber Standardization and Flow Checks**

Before and after each welding test run, the air flow rate through the welding test chamber and sample filters shall be verified to be between 709 and 989 liters per minute as specified in AWS F1.2:2006. These flow checks must be documented in the Test Run Data Log. This flow rate verification will document that there is sufficient flow through the welding test chamber to carry the emissions to the filter.

The exhaust flow rate will be monitored to ensure that the flow through the chamber does not drop below the minimum 25 CFM specified in AWS F1.2:2006. The purpose of this requirement is to ensure that all fumes are drawn up through the filter where it is captured, and that none of the fume escapes through the access ports or the bottom of the chamber. Reproducibility of the mass of fume captured/mass of electrode consumed for each process/electrode combination shall be calculated upon receiving the gravimetric results from the lab. Reproducibility of the results, with a Relative Standard Deviation (RSD) of less than 20%, with a minimum of 3 data points from the mass of fume captured from a specific consumable, at specified welding parameters, will demonstrate that the system is in calibration. This data must be presented in the final report to indicate the combined precision of welding fume generation and fume capture.

Each run shall be timed from when the arc is ignited on the base metal to when the arc is extinguished as recommended by section 7.5 of the AWS F1.2:2006. This section of the AWS specification also explains that the weld times will vary because they will depend on the amount of fume generated which will increase the filter loading. If the filter becomes overloaded, fumes will no longer pass freely through the filter and will begin to escape out the sides of the chamber. To be confident that the entire fume is collected on the filter and that the filters are not overloaded, the welding should be stopped when the flow rate reaches 25 CFM, which is the minimum flow rate listed in section 4.2.3 of the AWS F1.2:2006. Test runs may be performed to determine the actual weld time that will be conducted. After the welding process is complete, the blower must remain on for one (1) additional minute to clear the chamber of all fumes. This exceeds the recommendation of Section 7.6 of the AWS F1.2:2006, which states that the blower should be left on for an additional 30 seconds after the welding has stopped.

## **10.2 Analytical Calibration/Standardization**

Laboratories shall adhere to the selected OSHA and NIOSH methodologies for the analysis of the samples collected during this testing. These methods provide requirements for the calibration and standardization of the analytical equipment.

## **11.0 ANALYTICAL PROCEDURES**

### **11.1 Gravimetric Analysis**

The samples collected on pre-weighed glass fiber filters and quartz fiber filters shall be returned to the same environmentally controlled laboratory where the filters were pre-weighed before the sampling event. The analytical laboratory will record the post weights on these samples using the NIOSH Manual of Analytical Methods (NMAM) 0500 method for gravimetric analysis. A copy of the NMAM 0500 method is included in Appendix E for reference.

### **11.2 Total Metals Analysis**



Upon completion of the NIOSH 0500 gravimetric analysis, the glass fiber filters shall be digested and analyzed in accordance with the NIOSH 7300 *Elements by ICP* (Nitric/Perchloric Acid Ashing), adjusting solution volumes and dilutions as necessary for the filter size, total fume mass, and expected metals mass of the filtrate. One major modification to the test method is that the 8” filters must be cut in half by the lab and each half digested separately. Equal portions of the two (half-filter) digested solutions shall be mixed together before analysis. A detailed description of the actual sample preparation procedure is included in Appendix C.

### 11.3 Hexavalent Chromium Analysis

The quartz fiber filters quenched in the field with the 10% Na<sub>2</sub>CO<sub>3</sub>/NaHCO<sub>3</sub> solution will be analyzed for Cr(VI) in accordance with the OSHA ID-215 *Hexavalent Chromium* method. This method uses alkaline extraction condition which prevents the reduction of Cr(VI) to Cr(III), and includes the addition of phosphate buffer/magnesium sulfate to the extraction media to reduce interferences from iron (II). In addition, it is an ion chromatography method with post column derivatization and detection by visible spectroscopy. The combination of these two techniques makes the method very specific for Cr(VI). The quantitative detection limit for this method is 0.003 µg/m<sup>3</sup>. Solution volumes and dilutions are to be adjusted as necessary for the filter size, total fume mass, and expected metals mass of the filtrate. A detailed description of the actual sample preparation procedure is included in Appendix B.

## 12.0 CALCULATIONS AND DATA ANALYSIS

### 12.1 Calculation of Electrode Usage

#### 12.1.1 SMAW – Calculation for Stick Electrode Mass

$$\text{Grams of Electrode Consumed} = (\text{mass of rod}_{\text{initial}}) - (\text{mass of rod}_{\text{final}})$$

#### 12.1.2 FCAW/GMAW – Calculation for Wire Electrode Mass

When using wire electrodes for FCAW and GMAW, the wire feed speed in “inches per minute” is to be determined, along with the wire unit weight in “grams per inch”. To determine this, wire must be run from the gun for 15 seconds, with no welding occurring. The length of the wire must be documented on the “Test Run Data Log Sheets” included as Appendix D. This must be repeated 4 times, and an overall average length of wire, in inches per 15 seconds, must be calculated. The average length of wire discharged over 15 seconds is then entered into the equation presented in Section 12.1.3 below, which will provide a value in inches of wire per minute. The total section of wire that is discharged must be weighed, so that a weight in grams per inch of wire can be calculated. In addition to the wire information, the welding times must also be recorded. Using this information, the mass of weld wire consumed for each test run can be calculated using the following equations:

### 12.1.3 FCAW/GMAW – Calculation for Wire Feed Speed

$$\text{Inches of wire per minute} = \frac{\text{inches of wire}}{15 \text{ seconds}} \times \frac{60 \text{ seconds}}{1 \text{ minute}}$$

### 12.1.4 FCAW/GMAW – Calculation for Wire Electrode Mass

$$\text{Grams Wire Consumed} = \frac{\text{inches of wire}}{\text{minute}} \times \frac{\text{grams of wire}}{\text{inch}} \times \text{minutes of welding}$$

## 12.2 Calculation of Emission Factors

The emissions factors for total fume shall be calculated in units of grams/kilogram of electrode consumed, so that they will be consistent with emissions factors reported in AP-42.

$$\text{Total Fume Emission Factor} = \frac{\text{grams of total fume}}{\left(\frac{\text{grams of electrode consumed}}{1000}\right)}$$

The emissions factors for hazardous air pollutants (HAPs) shall be calculated in units of  $10^{-1}$  grams/kilogram of electrode consumed, so that they will be consistent with emissions factors reported in AP-42.

$$\text{HAP Emission Factor} = \frac{\left(\frac{\text{grams of metal in fume}}{10}\right)}{\left(\frac{\text{grams of electrode consumed}}{1000}\right)}$$

## 13.0 POLLUTION PREVENTION

The filters used in the fume chamber are designed to capture 99.9% of the particulates from the exhaust air stream. It is recommended that a local exhaust ventilation system with a High-Efficiency Particulate Air (HEPA) filtration system be placed at the exhaust of the fume chamber blower to capture the exhaust air. This will ensure that any hazardous particulates are captured in the event that the filter fails in the chamber.

## 14.0 WASTE MANAGEMENT

### 14.1 Material Disposal

It is recommended that all base metals used in this study be recycled by a scrap metal recycler.

## 14.2 Sample Disposal

Laboratories will be responsible for the proper disposal of any remaining samples after the metals analysis has been completed through their standard sample disposal procedures.

## 15.0 REFERENCES

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**APPENDIX A**

**Weld Fume Chamber Manual**

**APPENDIX B**

**OSHA ID-215 and Laboratory Modifications**

## **Contract Analytical Lab Sample Preparation for Hexavalent Chromium on 8" Quartz Fiber Filters**

Samples were prepared by placing 8" Quartz-fiber filters face-down in 9 inch Pyrex pie plates. Sixty (60) mL of extraction solution and 18 mL of phosphate buffer/Mg II solution were added to each sample as per OSHA ID-215 (mod). Samples were covered with a 12 inch platter watch glass and heated for at least 30 minutes at 100 °C to 110 °C in a Blue M Stable-Therm Gravity Oven, with occasional swirling. Samples were allowed to cool, transferred quantitatively to 200 mL volumetric flasks, and brought to volume with ASTM type II water. Each sample was then filtered with Gelman 0.45 µm Ion Chromatography Acrodiscs into 1.8 mL amber autosampler vials prior to analysis.

HEXAVALENT CHROMIUM IN WORKPLACE ATMOSPHERES




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OSHA Method Number:	ID-215 (This method supersedes ID-103)
Matrix:	Air
OSHA Permissible Exposure Limit (proposed)	
Hexavalent Chromium [Cr(VI)]	
Time Weighted Average (TWA):	0.50 µg/m <sup>3</sup>
Action Level (AL):	0.25 µg/m <sup>3</sup>
Collection Device:	An air sample is collected using a 37-mm diameter polyvinyl chloride (PVC) filter (5-µm pore size) contained in a polystyrene cassette. A calibrated sampling pump is used to draw a representative air sample from the breathing zone of an employee through the cassette and collect particulate on the filter.
Recommended Sampling Rate:	2 liters per minute (L/min)
Recommended Air Volume:	
TWA and AL:	960 L (2 L/min for 480 min)
Analytical Procedure:	The hexavalent chromium, Cr(VI), is extracted from the PVC filter using an aqueous solution containing 10% sodium carbonate (Na <sub>2</sub> CO <sub>3</sub> )/ 2% sodium bicarbonate (NaHCO <sub>3</sub> ) and the mixture of phosphate buffer/magnesium sulfate [- 10 mg as Mg (II)]. After dilution, an aliquot of this solution is analyzed for Cr(VI) by an ion chromatograph equipped with a UV-vis detector at 540-nm wavelength. A post-column derivatization of the Cr(VI) with 1,5-diphenyl carbazide is performed prior to detection.
Detection Limit	
Qualitative:	1.0 × 10 <sup>-3</sup> µg/m <sup>3</sup> as Cr(VI) (960-L air sample)
Quantitative:	3.0 × 10 <sup>-3</sup> µg/m <sup>3</sup> as Cr(VI) (960-L air sample)
Precision and Accuracy (Soluble and Insoluble)	
Validation Range:	0.12 to 0.42 µg/m <sup>3</sup> (960-L air sample)
CV <sub>1</sub> (pooled):	0.059
Bias:	- 0.004
Overall Error:	±12.9%
Method Classification:	Validated Method
Chemists:	James C. Ku, Mary Eide
Date:	June, 1998

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Commercial manufacturers and products mentioned in this method are for descriptive use only and do not constitute endorsements by USDOL-OSHA. Similar products from other sources can be substituted.

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Branch of Inorganic Methods Development  
 OSHA Salt Lake Technical Center  
 Salt Lake City, Utah



## 1. Introduction

This method describes the sample collection and analysis of airborne hexavalent chromium, Cr(VI). This method should be used by industrial hygienists experienced in monitoring for exposures and analysts experienced in the use of ion chromatography and the interpretation of ion chromatograms. Samples are taken in the breathing zone of workplace personnel, and analysis is performed with an ion chromatograph (IC) equipped with a UV-vis detector and a postcolumn reagent delivery system. Hexavalent chromium most commonly exists in the workplace as a metal (M) chromate ( $M\text{CrO}_4$ ), such as lead chromate, or also as chromium trioxide ( $\text{CrO}_3$ ). Common interferences noted in past methods, such as Cr (III) and Fe(II) are kept to a minimum.

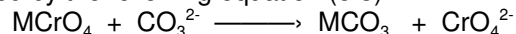
### 1.1 History

To sample for Cr(VI) in the workplace, a 37-mm diameter, 5- $\mu\text{m}$  pore size polyvinyl chloride (PVC) filter is normally used as the sampling medium. The classical method of Cr(VI) analysis for industrial hygiene use was colorimetry using 1,5-diphenylcarbazide (DPC) for color development after acid extraction of the Cr(VI) from the sample (5.1, 5.2). This method was considered inadequate due to the insolubility of certain chromate compounds (5.3) and interferences from many heavy metals (5.2). In addition, reducing agents, such as Fe(II), could convert the Cr(VI) to Cr(III) in the acidic extraction medium used (5.4). To avoid reduction of Cr(VI) in acidic media, alternatives were researched. The extraction of Cr(VI) in basic solution, acidification, and subsequent analysis by colorimetry using DPC has been reported in the literature (5.3). This method took advantage of the fact that all soluble chromates and many of the insoluble chromates can be extracted in a basic solution (5.3, 5.7). However, the potential still existed for positive interferences. Also, Cr(VI) could be converted to Cr(III) by a reducing agent such as Fe(II) in the basic medium. To minimize these problems, a differential pulse polarographic (DPP) method was developed (5.8) at the OSHA Salt Lake Technical Center (SLTC). The buffer used for sample extraction in the DPP method, 10%  $\text{Na}_2\text{CO}_3$  and 2%  $\text{NaHCO}_3$  was a modification of that suggested in Reference 5.3. This buffer was also used as the supporting electrolyte during analysis.

Recently, a reduction in the Permissible Exposure Limit (PEL) for Cr(VI) has been proposed by OSHA, with 0.50  $\mu\text{g}/\text{m}^3$  for the Time Weighted Average (TWA) and 0.25  $\mu\text{g}/\text{m}^3$  for the Action Level (AL). The differential pulse polarographic method was not sufficiently sensitive to quantitate at the proposed levels, and a new method was developed using an IC equipped with a UV-vis detector and a postcolumn reagent delivery module. To prevent interferences, the Cr(VI) ion is separated from other analytes using an ion chromatographic column. The Cr(VI) then reacts with the DPC to form a colored derivative which is measured by the UV-vis detector at 540 nm. A significant increase in sensitivity for Cr(VI) is noted when compared to previous methods. Initial studies, performed using only a hot 10% sodium carbonate 2% sodium bicarbonate solution for extraction, still demonstrated a negative interference from Fe(II) and some conversion of Cr (III) to Cr(VI). Next we evaluated the modification presented by Vitale et al. and Zátka to inhibit the oxidation of Cr(III) to Cr(VI), whereby magnesium hydroxide was freshly precipitated in the carbonate buffer by the addition of a magnesium chloride solution (5.5, 5.6). The studies in this method showed that the addition per sample of ~10 mg Mg(II) in a phosphate buffer to the 10% sodium carbonate 2% sodium bicarbonate solution greatly decreased the negative interference of the Fe(II) and positive interference of the Cr(III).

### 1.2 Principle

Hexavalent chromium is collected on a 37-mm diameter PVC filter. Any compound existing in the Cr(VI) valence state is extracted from the PVC filter using a hot aqueous solution containing 10% sodium carbonate ( $\text{Na}_2\text{CO}_3$ ), 2% sodium bicarbonate ( $\text{NaHCO}_3$ ), and the phosphate buffer/magnesium sulfate mixture. The reaction between any chromate species and carbonate is illustrated by the following equation (5.3):



Where M = metals (e.g., lead, zinc, cadmium, sodium, potassium, calcium, etc.)

In the presence of a large excess of carbonate, the equilibrium is shifted quantitatively to the right. Any chromate compounds (soluble and insoluble) contained in the sample are converted to their corresponding soluble carbonates. Interferences are minimized by the addition of the magnesium.

After dilution, an aliquot of this extract is analyzed for Cr(VI) with an IC equipped with a postcolumn reagent delivery module and a UV-vis detector at 540-nm wavelength. Any Cr(VI) in a spray-paint sample on the filter is extracted additionally with a hot 5% NaOH/7.5% Na<sub>2</sub>CO<sub>3</sub> extraction solution with the mixture of phosphate buffer/Mg(II) (see Section 3.5.7). Using a well-buffered ammonium sulfate [(NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub>] and ammonium hydroxide (NH<sub>4</sub>OH) eluent, Cr(VI) is chromatographed as the yellow divalent CrO<sub>4</sub><sup>2-</sup> anion on the separator column. After the separation, Cr(VI) reacts with the reagent DPC to form a colored complex ion. The reaction is apparently the simultaneous oxidation of DPC to diphenylcarbazone and reduction of Cr(VI) to Cr(III). The actual structure of the chelate is not known, but the reaction is quantitative and the visible absorbance can be detected using a photometric detector at 540 nm (5.12). Although DPC, as previously stated, has the potential problem of reacting with other species, the addition of the chromatographic separation step minimizes any potential for interferences.

### 1.3 Advantages and Disadvantages

- 1.3.1 This method has adequate sensitivity for determining compliance with the proposed OSHA TWA and AL PELs for Cr(VI) exposure.
- 1.3.2 The method is simple, rapid, and easily automated.
- 1.3.3 The method is specific and can determine Cr(VI) in the presence of Cr(III). Most heavy metals, such as vanadium, copper, iron (III), and molybdenum, do not significantly interfere. Fe(II) appears to cause a negative interference during sampling and storage (see Sections 1.5 and 4.4 for further information).
- 1.3.4 By using alkaline extraction conditions (pH = 10 to 11) in which Cr(VI) is more stable, 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 the alkaline (carbonate/ bicarbonate/Mg(II)/phosphate) buffer. The extraction medium specified in this method minimizes the possible interferences.
- 1.3.5 Extraction and preparation of samples for analyses involve simple procedures and equipment.
- 1.3.6 If necessary, the amount of Cr(VI) can also be analyzed and confirmed by differential pulse polarography (DPP), provided samples and standards are matrix-matched. This DPP technique is described in reference 5.8.
- 1.3.7. A disadvantage is the extraction solution and sulfuric acid used are very caustic. The extraction solution may also limit the column life and type of instrumentation used. The module used in this method is equipped with a reagent reservoir, a mixing tee/reaction coil system, and a post-column pneumatic controller. A Dionex membrane reactor was used during early stages of validation of this method. The mixing tee and reaction coil used in subsequent studies was found more suitable because the Dionex membrane reactor required: a) frequent maintenance; b) additional dilution of sample standards to minimize matrix effects from the extraction solution (resulting in a corresponding decrease in sensitivity); and c) greater expense. The mixing tee and reaction coil only require a 1:1 dilution prior to analysis.

### 1.4 Method Performance

A synopsis of the method performance is presented below. Further information can be found in Section 4.

- 1.4.1 This method was validated using soluble and insoluble chromate compounds. The compounds used were potassium dichromate and lead chromate for soluble and insoluble chromate, respectively. The significant availability and industrial use of potassium dichromate indicated it was a good choice to represent the chemical characteristics of the

soluble chromates for this evaluation. Solubility product values indicated that lead chromate was the least soluble of the chromate compounds commonly found in industry, therefore it was chosen to represent the insoluble chromate. Filter samples were spiked with about 0.11 to 0.40 µg [as Cr(VI)]. Using an 960-L air volume, these spiked samples would give an approximate concentration range of 0.115 to 0.417 µg/m<sup>3</sup> as Cr(VI). This method has the sensitivity necessary to determine compliance with the proposed regulatory limits.

- 1.4.2 The qualitative detection limit was 0.001 µg as Cr(VI) when using a 10-mL solution volume. This corresponds to  $1.0 \times 10^{-3}$  µg/m<sup>3</sup> as Cr(VI) for a 960-L air volume.
- 1.4.3 The quantitative detection limit was 0.003 µg as Cr(VI) when using a 10-mL solution volume. This corresponds to  $3.0 \times 10^{-3}$  µg/m<sup>3</sup> as Cr(VI) for a 960-L air volume. A 100-µL sample loop and a detector setting of 0.5 absorbance unit (AU) full-scale output were used for both qualitative and quantitative detection limits.
- 1.4.4 The sensitivity of the analytical method, when using the instrumental parameters listed in Section 3.6., was calculated from the slope of a linear working range curve [0.5 to 1,000 ng/mL Cr(VI)]. The sensitivity was  $2.47 \times 10^4$  area units per 1 ng/mL, when using a Dionex Series 4500i ion chromatograph with AI450 computer software (Dionex, Sunnyvale, CA). The sensitivity was  $1.57 \times 10^4$  area units per 1 ng/mL, when using a Dionex DX500 ion chromatograph with a 10 mm cell and a 150 µL sample loop (Dionex, Sunnyvale, CA). The sensitivity of this method was significantly better than OSHA Method No. ID-103 for Cr(VI) (5.8).
- 1.4.5 The total pooled coefficients of variation (CV<sub>1</sub>), bias, and total overall error (OE) are as follows:

For soluble chromate:  
 CV<sub>1</sub> (pooled) = 0.054; bias = + 0.007; OE<sub>T</sub> = ±11.5%

For insoluble chromate:  
 CV<sub>1</sub> (pooled) = 0.064; bias = - 0.014; OE<sub>T</sub> = ±14.2%

For both types of chromate compounds (pooled soluble and insoluble):  
 CV<sub>1</sub> (pooled) = 0.059; bias = - 0.004; OE<sub>T</sub> = ±12.9%

- 1.4.6 The collection efficiency of  $0.945 \pm 0.035$  has been previously determined for chromic acid mist collected on PVC filters (5.11).
- 1.4.7 Quality control (QC) samples were prepared as single blind samples by spiking aqueous solutions of potassium dichromate on PVC filters. Amounts spiked ranged from 10 to 20 µg. Results of samples analyzed from 1982-89 using the DPP technique, and samples analyzed using this method (IC/UV-vis) are shown below. All samples were analyzed along with other field (compliance) samples. The following results were obtained:

	<u>Method Used</u>	
	<u>DPP*</u>	<u>IC/UV-vis</u>
Samples (N):	282	57
Average recovery:	94.1%	94.8%
CV <sub>1</sub> (pooled):	0.10	0.054

\*DPP data obtained from reference 5.12.

- 1.4.8 Samples can be stored at ambient (20 to 25 °C) temperature on a lab bench for a period of at least 30 days. The mean sample recovery after 30 days of storage was within ±5% of the recovery at Day 0.

## 1.5 Interferences

- 1.5.1 Reducing species such as Cr(III), V(III), and Cu(I), etc. in ten-fold excess over Cr(VI) did not produce a significant interference with this method. However, when Fe(II) was added in a slightly acidic environment, and the samples were extracted with the BE solution, the following losses occurred: 10% for a loading of Fe(II):Cr(VI) of 1:1, 30% when 5:1, 70% when 10:1, and 3% for 10:1 with the addition of the Mg(II) and phosphate buffer before extraction with BE solution. The effects of this negative interference are further detailed in Section 4.4. The samples were extracted with the buffer extraction (BE) solution only. These losses were significantly reduced by the addition of magnesium sulfate ~10 mg/mL as Mg (II), in a phosphate buffer to the BE solution, such that a 1:10 ratio of Cr(VI):Fe(II) had an average recovery of 96.6% (see Section 4.4.6). Loss in basic solutions appeared to be independent of Cr(VI)/Fe(II) ratio.
- 1.5.2 A positive interference can be any substance that has the same retention time as Cr(VI), and absorbs light at 540 nm wavelength when using the ion chromatographic operating conditions described in this method. Changing the chromatographic separation conditions (detector settings, column, eluent flow rate, and strength, etc.) may minimize the interference. None of the more common metallic species coexisting with Cr(VI) in the workplace and potentially soluble in the extraction solution were found to positively interfere when using the analytical conditions described in this method. A positive interference from Cr (III) can occur when extracted with BE or a more strongly basic extraction solution for spray paint samples (SPE) alone; however, the addition of the phosphate buffer/Mg(II) solution to the extraction process minimizes this positive interference. For samples having Cr(III) levels of 1 µg/mL, the positive interference changed from <1% for BE to <0.02% for BE with phosphate buffer/Mg(II). For SPE samples containing 10 µg/mL Cr(III), the positive interference changed from <0.2% for SPE to <0.03% for SPE with phosphate buffer/Mg(II) (see Sections 4.4.1, 4.4.3, and 4.4.4).

## 1.6 Uses

The principal commercial Cr(VI) compounds are chromium trioxide (chromic acid anhydride), and the chromates and dichromates of sodium, potassium, ammonium, calcium, barium, zinc, strontium, and lead. They are used as oxidizing agents in tanning, photography, dyeing, and electroplating, and as rust inhibitors and pigments.

## 1.7 Physical and Chemical Properties of Certain Chromates (5.15)

	Chromium (VI) trioxide	Potassium chromate	Lead chromate	Zinc chromate	Potassium dichromate
CAS No.	1333-82-0	7789-00-6	7758-97-6	13530-65-9	7778-50-9
Synonyms	Chromic acid, chromic anhydride; Chromia; Chromic trioxide	Chromic acid, dipotassium salt; Dipotassium monochromate	Chromic acid, lead salt; Crocoite; Phoenicochroite; Plumbous chromate	Chromic acid, zinc salt; Zinc tetraoxochromate; Zinc chromium oxide	Potassium bichromate; red potassium chromate
Description	Dark, purple-red crystals	Rhombic, yellow crystals	Yellow crystals	Lemon-yellow prisms	Yellow-red crystals
Formula	CrO <sub>3</sub>	K <sub>2</sub> CrO <sub>4</sub>	PbCrO <sub>4</sub>	ZnCrO <sub>4</sub> *	K <sub>2</sub> Cr <sub>2</sub> O <sub>7</sub>
Constants and Solubility	Mol wt: 100.01 mp: 196 °C d: 2.70 Very sol in water (625 g/L at 20 °C), insol in alcohol.	Mol wt: 194.20 mp: 971 °C d: 2.732 at 18 °C Sol in water (1,020 g/L at 100 °C), insol in alcohol.	Mol wt: 323.22 mp: 844 °C bp: decomposes d: 6.3 Very slightly sol in water (0.058 mg/L at 25 °C), sol in strong acids and alkalis.	Mol wt: 181.4 mp: not available d: 3.40 Slightly sol in water, sol in acids.	Mol wt: 294.2 mp: 396 °C decomposition pt: 500 °C d: 2.676 Sol in water (1.020g/L @ 100 °C) insol in alcohol
Fire and explosion hazard	Dangerous: a very powerful oxidizing agent. In contact with organic matter or reducing agents in general it can cause violent reactions. Upon intimate contact with powerful reducing agents it can cause violent explosions.	Moderate, by chemical reaction; a powerful oxidizer.	Moderate, by chemical reaction.	Moderate, by chemical reaction.	Moderate, by chemical reaction

\*Molecular formula was 4ZnO·CrO<sub>3</sub>·3H<sub>2</sub>O, and confirmed in-house by X-ray diffraction.

## 1.8 Toxicology (5.16)

Information listed within this section is a synopsis of current knowledge of the physiological effects of chromic acid and chromates and is not intended to be used as a basis for OSHA policy.

- 1.8.1 Chromic acid and its salts have a corrosive action on the skin and mucous membranes. The characteristic lesion is a deep, penetrating ulcer, which, for the most part, does not tend to suppurate, and is slow in healing. Lesions are confined to the exposed area, and the skin of the nasal septum is a common site.
- 1.8.2 Breathing in high levels (greater than 2 µg/m<sup>3</sup>) of Cr(VI) can cause irritation to the nasal passage, such as runny nose, sneezing, itching, nosebleeds, ulcers, and holes in the nasal septum. These effects have primarily occurred in factory workers who have produced or used Cr(VI) for several months to many years. Long-term exposure to Cr(VI) has been associated with lung cancer in workers exposed to high levels of Cr(VI) in workplace air.
- 1.8.3 Workers handling liquids or solids containing Cr(VI) compounds have developed skin ulcers.
- 1.8.4 Certain Cr(VI) compounds (calcium chromate, chromium trioxide, lead chromate, sodium dichromate, strontium chromate, and zinc chromate) are known animal and/or human carcinogens. The International Agency for Research on Cancer (IARC) has determined that Cr(VI) is carcinogenic to humans (Group 1), based on sufficient evidence in humans

for the carcinogenicity of Cr(VI) compounds as found in chromate production, chromate pigment production, and chromium plating industries (5.17). IARC's determination is also based on sufficient evidence in experimental animals for the carcinogenicity of calcium chromate, zinc chromate, strontium chromate, and lead chromate; and limited evidence in experimental animals for the carcinogenicity of chromic acid and sodium dichromate.

## 2. Sampling (See Interferences, Section 1.5 before sampling.)

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Note: Bulk samples can be collected and analyzed. Filters or wipe samples collected on cellulose or cellulose esters are unacceptable due to the instability of Cr(VI) on these media.

Filter media used to validate this chromate method and to prepare QC samples are the PVC filters manufactured by MSA Inc. and Omega Special Instrument Co. as specified below. The Gelman GLA-5000 was also evaluated for extraction and storage and found acceptable. If a PVC filter from a different manufacturer is used, it will be necessary to at least evaluate the extraction efficiency and the storage, as it has been reported that there are interferences on some types of PVC filters which greatly reduce the hexavalent chromium to trivalent chromium.

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### 2.1 Equipment

- 2.1.1 Calibrated personal sampling pumps capable of sampling within  $\pm 5\%$  of the recommended flow rate of 2 L/min.
- 2.1.2 Tygon or other flexible tubing for connecting to pumps.
- 2.1.3 Plastic end plugs.
- 2.1.4 Sample assembly:
  - a) Filter holder consisting of a two-piece polystyrene cassette, 37-mm diameter.
  - b) Backup pad, 37-mm, cellulose.
  - c) Membrane filter, PVC, 37-mm, 5- $\mu\text{m}$  pore size [part no. 625413, Mine Safety Appliances (MSA), Pittsburgh, PA; or cat. no. P-503700, Omega Specialty Instrument Co., Chelmsford, MA].
  - d) Gel bands (Omega Specialty Instrument Co., Chelmsford, MA) for sealing cassettes.
  - e) Forceps, Teflon coated.
- 2.1.5 Stopwatch and bubble tube or meter for pump calibration.
- 2.1.6 Scintillation vials (for wipe or bulk samples), 20-mL, part no. 74515 or 58515, (Kimble, Div. of Owen-Illinois Inc., Toledo, OH) with polypropylene or Teflon cap liners.

### 2.2 Sampling Procedure - Air Samples

- 2.2.1 Place a PVC filter and a cellulose backup pad in each two-piece cassette. Compress the cassette and then seal each cassette with a gel band. The atmosphere being sampled should pass through the PVC filter first.
- 2.2.2 Calibrate each personal sampling pump with a prepared cassette in-line to approximately 2 L/min flow rate.
- 2.2.3 Attach prepared cassettes to calibrated sampling pumps (the backup pad should face the pump) using appropriate lengths of tubing. Place each cassette within the breathing zone on each employee as appropriate. If possible, collect each sample for a full work shift (approximately 960-L air volume).

- 2.2.4 If the filter becomes overloaded while sampling, consecutive samples using shorter sampling periods should be taken.
- 2.2.5 After sampling, place plastic end caps tightly on both ends of the cassette and apply OSHA Form 21 seals in such a way as to secure the end caps. Record the sampling conditions such as sampling time, air volume, etc. on the OSHA 91A form. **(Note: It is very important to record the operation sampled (i.e., spray paint, chrome plating, welding, etc.))** When other compounds are known or suspected to be present in the air, record such information and transmit with the samples.
- 2.2.6 Use the same lots of filters and backup pads for blanks and collected samples. Handle the blank cassettes in exactly the same manner as the sample cassettes except that no air is drawn through them. Submit at least one blank cassette for each batch of ten samples.

### 2.3 Sampling Procedure - Wipe Samples

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

### 2.4 Sampling Procedure - Bulk Samples

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.

### 2.5 Shipment

- 2.5.1 Immediately send the samples to the laboratory with the OSHA 91A paperwork requesting hexavalent chromium [Cr(VI)] analysis.
- 2.5.2 Ship any bulk samples separately from air samples. Enclose Material Safety Data Sheets if available. Check current shipping restrictions and ship to the laboratory by the appropriate method and proper labeling.

## 3. Analysis

### 3.1 Safety Precautions

- 3.1.1 Refer to appropriate IC instrument manuals, UV-vis detector maintenance manual, and any Standard Operating Procedures (SOP) for proper instrument operation (5.19).
- 3.1.2 Observe laboratory safety regulations and practices.
- 3.1.3 Certain chromate compounds have been identified as carcinogens (5.16, 5.17). Care should be exercised when handling these compounds.
- 3.1.4 Some chemicals are corrosive. Use appropriate personal protective equipment such as safety glasses, goggles, face shields, gloves, and lab coat when handling corrosive chemicals.
- 3.1.5 The buffer/extraction (BE) and spray-paint extraction (SPE) solutions are basic and somewhat corrosive. Clean up any spills immediately. Store these solutions in polyethylene bottles. If the solutions are stored in glass, precipitated salts readily form over time from evaporation and will cause glass stoppers to seize. The strongly basic solutions will also attack the glass walls of the containers. Samples placed in glass volumetric flasks

should be analyzed, properly disposed of, and the flasks rinsed and washed as soon as possible after analysis is completed and results are reported.

## 3.2 Equipment

- 3.2.1 Ion chromatograph (Model 4000i, 4500i, or DX500 Dionex, Sunnyvale, CA) equipped with a UV/vis detector and a postcolumn reagent delivery system containing a pressurized reagent reservoir with a 1-L polyethylene bottle, a post column pneumatic controller, and a mixing tee and reaction coil (Note: A membrane reactor module can be used in place of a mixing tee and reaction coil; however, extra maintenance is required, and depending on the module, additional dilution of the sample prior to analysis may be necessary.).
- 3.2.2 Hot plate and exhaust hood.
- 3.2.3 For extraction of air samples, use Phillips beakers, borosilicate, 125-mL, with watch glass covers, or Erlenmeyer flasks, 50-mL. It is recommended that the beakers or flasks used for extraction of bulks be of a larger size (250 mL has been used) than the beakers or flasks used for air samples, to help prevent contamination of air samples from improperly cleaned glassware which may have contained high levels of Cr (VI). Glassware which should not be used for sample analysis of chromate compounds are those:
  - 1) previously cleaned with chromic acid cleaning solution,
  - 2) previously used for storage of Cr(VI) stock standard solutions, and
  - 3) previously used for storage of bulks containing high concentrations of Cr(VI).
- 3.2.4 Teflon-coated magnetic stirring bar and stirrer, or ultrasonicator.
- 3.2.5 Micro-analytical balance (0.01 mg).
- 3.2.6 Polyethylene bottles, 100-mL to 1-L size with caps with plastic liners.
- 3.2.7 Calibrated micro-pipettes or pipets, volumetric flasks, beakers, and general laboratory glassware. The calibration on the micro-pipettes should be checked before each use. Alternately serial dilutions may be made using volumetric pipets.
- 3.2.8 Automatic sampler (Dionex Model AS-1) and sample vials (0.5 mL) with filter caps.
- 3.2.9 Laboratory automation system: Ion chromatograph interfaced with a data reduction system (AI450, Dionex).
- 3.2.10 Separator and guard columns, anion (Model IonPac-AS7 and IonPac-NG1, Dionex).
- 3.2.11 Syringe prefilters, 0.5- $\mu$ m pore size (part no. SLSR 025 NS, Millipore Corp., Bedford, MA).

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Note: Some syringe prefilters are not cation- or anion-free. Tests should be performed with blank solutions first to determine contamination and suitability with the analyte.

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- 3.2.12 Scintillation vials, glass, 20-mL.
  - 3.2.13 Equipment for eluent degassing (vacuum pump, ultrasonic bath).
  - 3.2.14 Optional: Centrifuge for spinning down precipitate in samples.
- 3.3 Reagents - All chemicals should be at least reagent grade. Consult latest material safety data sheets (MSDS) for cautions and proper handling.



### 3.3.1 Principal reagents:

Sodium carbonate ( $\text{Na}_2\text{CO}_3$ ), 99%  
Sodium bicarbonate ( $\text{NaHCO}_3$ ), 99%  
Potassium dichromate ( $\text{K}_2\text{Cr}_2\text{O}_7$ ), 99.9% or Potassium chromate ( $\text{K}_2\text{CrO}_4$ ), 99.9%  
Magnesium sulfate, anhydrous ( $\text{MgSO}_4$ ), 99%  
Ammonium sulfate [ $(\text{NH}_4)_2\text{SO}_4$ ], 99+%  
Ammonium hydroxide ( $\text{NH}_4\text{OH}$ ), 29%  
1,5-Diphenylcarbazide (DPC) -  $\text{C}_6\text{H}_5\text{NHNHCONHNHC}_6\text{H}_5$ , 99%  
Methanol ( $\text{CH}_3\text{OH}$ ), HPLC grade  
Sulfuric acid ( $\text{H}_2\text{SO}_4$ ), concentrated (98%)  
Nitric acid ( $\text{HNO}_3$ ), concentrated (69 - 71%)  
Deionized water (DI  $\text{H}_2\text{O}$ )

The initial studies were performed using magnesium chloride as the source of magnesium, but this formed a very fine precipitate of magnesium hydroxide. The source of magnesium was switched to magnesium sulfate, because the magnesium sulfate formed a larger sized precipitate which was easier to separate.

### 3.3.2 Nitric acid, 10% (v/v):

Carefully add 100 mL of concentrated  $\text{HNO}_3$  to about 500-mL DI  $\text{H}_2\text{O}$  contained in a 1.0-L volumetric flask and dilute to the mark with DI  $\text{H}_2\text{O}$ .

### 3.3.3 Buffer/extraction (BE) solution (10% $\text{Na}_2\text{CO}_3$ + 2% $\text{NaHCO}_3$ ):

Dissolve 100 g  $\text{Na}_2\text{CO}_3$  and 20 g  $\text{NaHCO}_3$  in about 500 mL DI  $\text{H}_2\text{O}$  contained in a 1.0-L volumetric flask. A Teflon-coated magnetic stirring bar and stirrer will facilitate dissolution. Remove and rinse the stirring bar, adding the rinses to the volumetric flask, and then dilute to the mark with DI  $\text{H}_2\text{O}$ . Alternately, a sonicator can be used instead of a stirring bar and stirrer. Transfer and store this solution in a tightly capped polyethylene bottle. Prepare monthly.

### 3.3.4 Spray-paint extraction (SPE) solution (5% $\text{NaOH}$ + 7.5% $\text{Na}_2\text{CO}_3$ ):

Dissolve 50 g  $\text{NaOH}$  and 75 g  $\text{Na}_2\text{CO}_3$  in about 500 mL DI  $\text{H}_2\text{O}$  contained in a 1.0-L volumetric flask. A Teflon-coated magnetic stirring bar and stirrer will facilitate dissolution. Remove and rinse the stirring bar, adding the rinses to the volumetric flask, allow the solution to cool to room temperature, and then dilute to the mark with DI  $\text{H}_2\text{O}$ . Alternately, a sonicator can be used instead of a stirring bar and stirrer. Transfer and store this solution in a tightly capped polyethylene bottle. Use this solution only for extraction of samples taken to assess exposure during spray-paint operations. Prepare monthly.

### 3.3.5 Magnesium sulfate solution [ $\sim 10$ mg/mL as $\text{Mg(II)}$ ]:

Dissolve 9.90 g of anhydrous  $\text{MgSO}_4$  in 100-mL volumetric flask containing 50 mL DI  $\text{H}_2\text{O}$ . Mix well and dilute to the mark with DI  $\text{H}_2\text{O}$ . Prepare monthly.

### 3.3.6 Phosphate buffer (0.5 M $\text{KH}_2\text{PO}_4$ /0.5 M $\text{K}_2\text{HPO}_4 \cdot 3\text{H}_2\text{O}$ ):

Dissolve 6.80 g of  $\text{KH}_2\text{PO}_4$  and 11.41 g of  $\text{K}_2\text{HPO}_4 \cdot 3\text{H}_2\text{O}$  in 100-mL volumetric flask containing 50 mL DI  $\text{H}_2\text{O}$ . Mix well and dilute to the mark with DI  $\text{H}_2\text{O}$ . Prepare monthly.

### 3.3.7 Phosphate buffer/ $\text{Mg(II)}$ (PBM) solution:

Pipette 25 mL of the magnesium sulfate solution (Section 3.3.5) into a 100-mL beaker containing 50 mL of phosphate buffer (Section 3.3.6). Mix well (Note: Do not dilute with DI  $\text{H}_2\text{O}$ ). Prepare just before each analysis.

3.3.8 Dilute Buffer Extraction/Phosphate buffer/Mg(II) or DBE/PBM solution [for working standard preparation (Section 3.4)]:

Pipette 50 mL of the BE solution (Section 3.3.3) into a 100-mL volumetric flask containing 15 mL of PBM solution (Section 3.3.7). Mix well and dilute to the mark with DI H<sub>2</sub>O. Magnesium hydroxide will form and precipitate out of solution. Allow the precipitation to settle for at least 60 min., or place in a centrifuge at 3,200 rpm for 10 min. Transfer the “clear” solution to a beaker. Prepare this solution just before working standard preparation.

3.3.9 Eluent [250 mM (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub> + 100 mM NH<sub>4</sub>OH]:

Dissolve 33 g of (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub> in about 500 mL of DI H<sub>2</sub>O. Add 6.5 mL of 29% NH<sub>4</sub>OH. Mix well and dilute with DI H<sub>2</sub>O to 1.0 L in a volumetric flask. Sonicate this solution and degas under vacuum for 5 min. Transfer the solution to the eluent container.

3.3.10 Postcolumn derivatization reagent (2.0 mM DPC + 10% CH<sub>3</sub>OH + 1N H<sub>2</sub>SO<sub>4</sub>):

1) First dissolve 0.5 g of DPC in 100 mL of HPLC grade CH<sub>3</sub>OH. 2) Add 28 mL of 98% H<sub>2</sub>SO<sub>4</sub> to about 500 mL of DI H<sub>2</sub>O (**CAUTION !!! Make additions very, very slowly, with mixing, and allow to cool.**) 3) Mix solutions 1) and 2) carefully and dilute, with stirring, in an 1-L volumetric flask with DI H<sub>2</sub>O. Cool solution to room temperature (**Caution: the reaction of the DPC with Cr(VI) will be incomplete if this solution is warm.**) Transfer the solution to the 1-L polyethylene bottle located in the pressurized reagent reservoir. The solution is stable for up to 3 days but should only be prepared as it is used, 1.0 L at a time. The sensitivity of the method is dependent on the freshness of the DPC solution.

3.3.11 Cr(VI) stock standard (100 µg/mL):

Dissolve and dilute 0.2828 g of K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub> or 0.3735 g of K<sub>2</sub>CrO<sub>4</sub> to 1.0 L with DI H<sub>2</sub>O. Prepare this solution every three months.

3.3.12 Cr(VI) standards (10.0 and 1.0 µg/mL):

To prepare 10.0 and 1.0 µg/mL Cr(VI) standards: 1) Pipette 12.5-mL BE solution into two 25-mL volumetric flasks. 2) Using a calibrated micropipette, pipette 2.5 and 0.25 mL of the 100 µg/mL Cr(VI) stock standard into each of the flasks. 3) Then dilute each flask to the mark with DI H<sub>2</sub>O. Prepare these solutions weekly. Alternately, volumetric pipets and 10-mL volumetric flasks may be used to prepare standards through serial dilutions.

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Note: The laboratory should have an effective, independent quality control (QC) program in place and QC samples of the analyte should be routinely analyzed along with field samples. Depending on the capabilities of the program, QC samples can either be generated using the collection media and chromate compounds under controlled conditions, or media can be spiked with the analyte (such as K<sub>2</sub>CrO<sub>4</sub> or K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub>). If QC samples cannot be routinely prepared and analyzed, two different standard stock solutions should always be prepared and these solutions should routinely be compared to each other. Always prepare the stocks from two different sources or, as last resort, from different lots.

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3.4 Working Standard Preparation - Prepare weekly.

Prepare Cr(VI) working standards in “clear” DBE/PBM solution. A suggested scheme for preparing a series of working standards using 10-mL final solution volumes and a calibrated micro-pipette is shown below, (the calibration on the micropipette should be checked on a monthly basis):

Working Std (ng/mL)	Std Solution ( $\mu\text{g/mL}$ )	Aliquot ( $\mu\text{L}$ )	DBE/PBM Added (mL)
1.0	1.0	10.0	9.99
5.0	1.0	50.0	9.95
10.0	1.0	100.0	9.90
20.0	10.0	20.0	9.98
50.0	10.0	50.0	9.95
100.0	10.0	100.0	9.90
200.0	100.0	20.0	9.98
500.0	100.0	50.0	9.95
1000.0	100.0	100.0	9.90

Serial dilutions with volumetric pipets and volumetric flasks may be used instead of a micropipette.

### 3.5 Sample Preparation

- 3.5.1 Wash all glassware in hot water with detergent and rinse with tap water, 10%  $\text{HNO}_3$ , and DI  $\text{H}_2\text{O}$  (in that order). **Caution: Under no circumstances should chromic acid cleaning solutions be used.**
- 3.5.2 Adjust the hot plate to a temperature below the boiling point of the BE solution. A plate surface temperature near  $135^\circ\text{C}$  is adequate for extraction. If the hotplate cannot be adjusted to  $135^\circ\text{C}$ , use a hot water bath.
- 3.5.3 If bulk samples are submitted, weigh out a representative aliquot of each bulk on separate PVC blank filters. The bulk and PVC filters are placed in a beaker or flask. To prevent potential future contamination, a beaker or flask of larger size than the air samples should be used.
- 3.5.4 Carefully remove each PVC filter from their cassettes or balance, place them face-down in separate 125-mL Phillips beakers (or 50-mL Erlenmeyer flask or other size of heat-resistant glassware used), add 1.5 mL of PBM solution, mix well, and finally add 5 mL of BE solution.

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Note: Always add PBM solution before adding the extraction solution. The freshly precipitated magnesium hydroxide [10 mg of  $\text{Mg(II)}$ ] formed suppresses the oxidation of dissolved  $\text{Cr(III)}$  to  $\text{Cr(VI)}$  (see Section 4.4. for details).

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Swirl the beaker slowly until the white precipitate occurs. Cover the beaker with a watch glass and very slowly heat the solution on the hot plate (surface temperature near  $135^\circ\text{C}$ ), with occasional swirling for 60 to 90 min. Allow extra extraction time for heavily loaded samples taken from spray-paint operations (See section 3.5.7). **DO NOT ALLOW ANY SOLUTIONS TO BOIL OR EVAPORATE TO DRYNESS.** Conversion of  $\text{Cr(VI)}$  to  $\text{Cr(III)}$  can occur from excess heat (5.4) causing loss of sample.

- 3.5.5 Allow the solutions to cool to room temperature. Quantitatively transfer each solution to a 10-mL volumetric flask using DI  $\text{H}_2\text{O}$ . Dilute to volume with DI  $\text{H}_2\text{O}$ .
- 3.5.6 If the solution is cloudy and/or other metal analyses are desired, filter the solution through a syringe prefilter. Alternately, cloudy samples may be centrifuged at 3,200 rpm for 10 min. to precipitate the  $\text{MgOH}$ . Avoid transferring any of the precipitate to the autosampler vials, as it will clog the IC autosampler, tubing, and/or column frits.
- 3.5.7. **FOR SAMPLES TAKEN FROM SPRAY-PAINTING OPERATIONS ONLY, PERFORM AN ADDITIONAL EXTRACTION OF EACH FILTER CONTAINING THE PAINT RESIDUE ACCORDING TO THE FOLLOWING PROCEDURE:**

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Note: Evidence indicates stronger base extractions are capable of recovering Cr(VI) in specific paint matrices (5.4). Due to the resistant properties of some industrial paints, an additional extraction is used for samples collected during spray-painting to assure complete recovery of all Cr(VI).

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- 1) After the initial extraction with BE and PBM, the solutions are transferred to 10-mL volumetric flasks. Place the sample beakers containing the remaining paint residue/filters and any blanks in an exhaust hood.
- 2) Add 1.5 mL of PBM solution and then 5 mL of SPE solution (Section 3.3.4) to each beaker containing the filters. Swirl the beaker slowly until a white precipitate occurs. Cover the beaker with a watch glass and very slowly heat the solution on the hot plate at 135°C, with occasional swirling for 60 to 90 min. Allow extra extraction time for heavily loaded samples. **DO NOT ALLOW ANY SOLUTIONS TO BOIL OR EVAPORATE TO DRYNESS.** Sample loss from the conversion of Cr(VI) to Cr(III) can occur from excess heat (5.4). Potential conversion of Cr(III) to Cr(VI) using a strong hydroxide extraction solution has also been noted (5.4). However, the freshly precipitated magnesium hydroxide [10 mg of Mg(II)] formed suppresses the oxidation of dissolved Cr(III) to Cr(VI) (see Section 4.4 for details).
- 3) Allow the solutions to cool to room temperature. Transfer each solution to a 25-mL volumetric flask. Dilute to volume with DI H<sub>2</sub>O. Allow the precipitate to settle, or centrifuge to segregate the precipitate to the bottom of the sample. Alternately, cloudy samples may be filtered through a syringe prefilter. It is important that none of the precipitate is transferred into the autosampler vials, as it can clog the IC autosampler, tubing, and/or column frits.

### 3.6 Analysis

- 3.6.1 Pipette a 0.5- to 0.6-mL “clear” portion of each standard or sample solution into separate automatic sampler vials (Note: Be careful not to transfer any of the milky-white magnesium hydroxide precipitate into the vials). Place a filtercap into each vial. The large filter portion of the cap should face the solution.
- 3.6.2 Load the automatic sampler with labeled samples, standards, and blanks.
- 3.6.3 Set up the ion chromatograph in accordance with the Standard Operating Procedure (SOP) (5.19). A diagram of the system flow path (adapted from Reference 5.12) is shown in Figure 1. Typical operating conditions for a Dionex 4000i, 4500i, or DX500 with a UV-vis detector and an automated sampler are listed below:

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Note: An SOP is a written procedure for a specific instrument. It is suggested that SOPs be prepared for each type of instrument used in a lab to enhance safe and effective operation.

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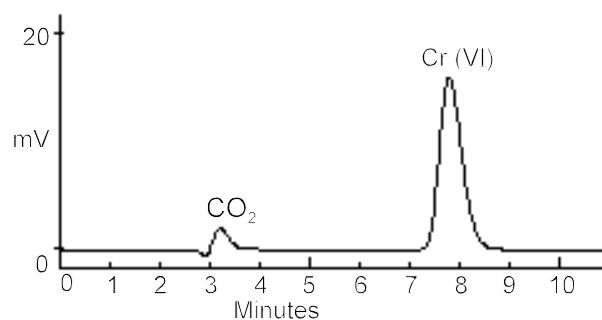
#### Ion Chromatograph

Eluent: 250 mM (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub> /100 mM NH<sub>4</sub>OH  
Postcolumn reagent: 2 mM DPC/10% CH<sub>3</sub>OH/1 N H<sub>2</sub>SO<sub>4</sub>  
Column temperature: ambient  
Anion precolumn: IonPac NG1  
Anion separator column: IonPac AS7  
Output range: 0.5 absorbance unit full scale (AUFS)  
Detection wavelength: 540 nm  
Sample injection loop: 100 µL (a 150 µL loop was used on the DX-500)

#### Pump

Pump  
pressure: ~950 psi  
Eluent flow rate: 0.7 mL/min

Postcolumn reagent  
flow rate: ~0.34 mL/min  
Chromatogram:



A chromatogram of 100 ng/mL Cr(VI).

The CO<sub>2</sub> peak is from the reaction of the bicarbonate and carbonate ions with the sulfuric acid in the post column derivatization mixture. The size of the CO<sub>2</sub> peak can be changed or eliminated by the amount of back pressure on the waste line coming from the detector.

Run time: 11 min  
Peak retention time: ~8 min for Cr(VI) (Please note that peak retention times are highly dependent on and individualized to the instrument in use and the age of the column.)

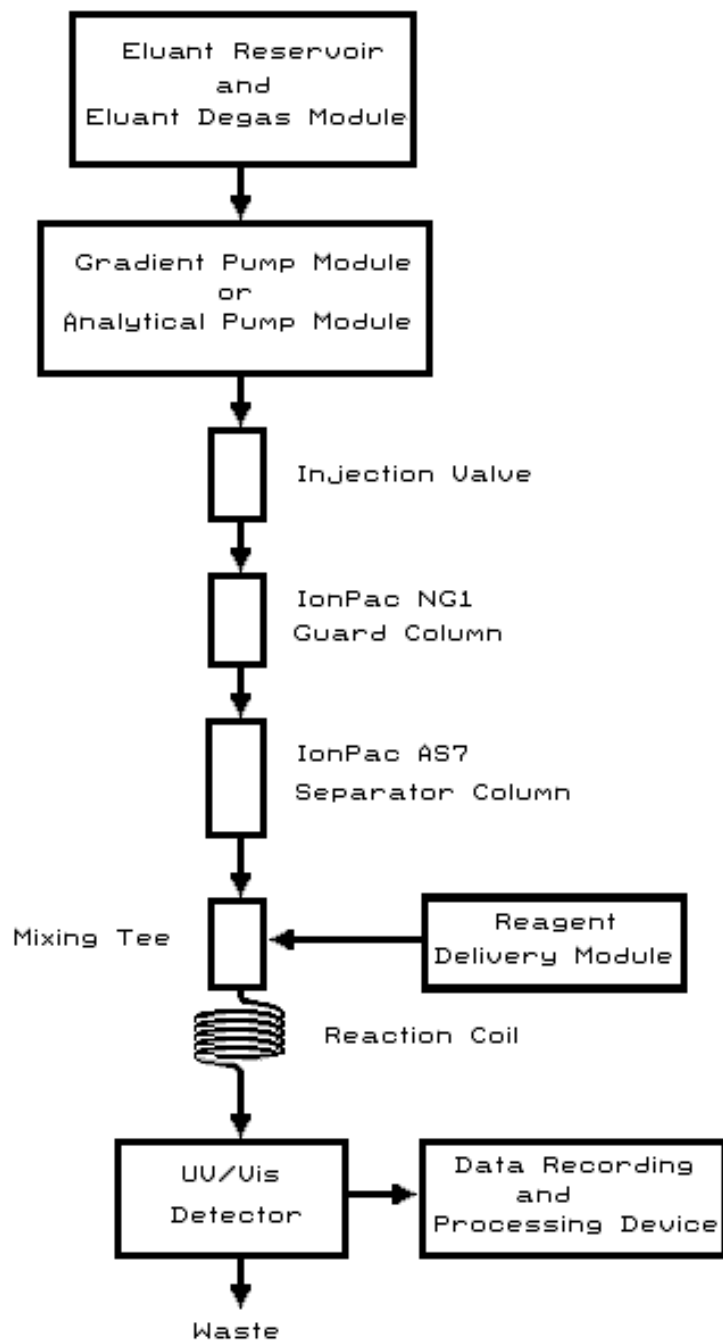


Figure 1. A diagram of the system flow path.

- 3.6.4 Follow the SOP for further instructions regarding analysis (5.19).
- 3.6.5 If any sample has a Cr(VI) concentration larger than the highest standard, dilute the sample by taking an appropriate aliquot and add an appropriate amount of DBE/PBM solution to bring the sample concentration within the range of the standards. A dilution factor (DF) as

calculated from the aliquot volume and diluent volume is used in final calculations (e.g., if a 2 mL aliquot is taken and 8 mL of DBE/PBM is added, then a DF of 5 is used.)

### 3.7 Calculations

- 3.7.1 After the analysis is completed, retrieve the peak areas or heights. Obtain hard copies of chromatograms from a printer.
- 3.7.2 Prepare a concentration-response curve by plotting the peak areas or peak heights versus the concentration of the Cr(VI) standards in ng/mL. Peak areas are preferred. Typical instrumental response for working standards from 10 to 1000 ng/mL range using a Dionex Model DX500 equipped with an AD20 Absorbance Detector and GP40 Gradient Pump as follows:

Level	Concentration ng/mL	Peak Height ( $\times 10^4$ )	Peak Area ( $\times 10^6$ )
1	0.500	0.005	0.015
2	1.000	0.010	0.031
3	5.000	0.051	0.152
4	10.00	0.095	0.279
5	20.00	0.190	0.545
6	50.00	0.491	1.422
7	100.0	0.980	2.803
8	200.0	1.858	5.245
9	500.0	4.522	12.363
10	1.000	9.628	24.736

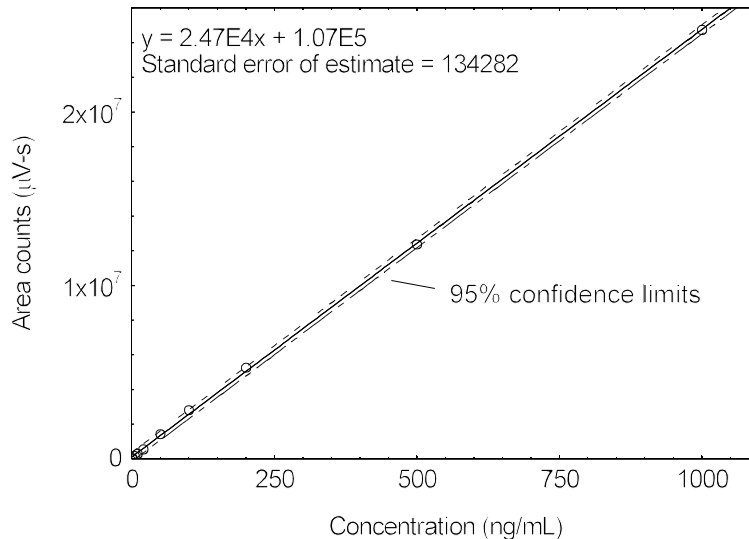


Figure 2. A plot of the standard curve of the above standards.

- 3.7.3 Perform a blank correction for each PVC filter result. Subtract the ng/mL Cr(VI) blank value (if any) from each sample reading if blank and sample solution volumes are the same. If a different solution volume is used, subtract the total ng blank value from each total ng sample value.

$$A_b = [\text{ng/mL Cr(VI)}]_b \times (\text{Sol Vol})_b$$

$$A_s = [\text{ng/mL Cr(VI)}]_s \times (\text{Sol Vol})_s$$

$$A = [A_s - A_b] \times DF$$

Then calculate the air concentration of Cr(VI) (in  $\mu\text{g}/\text{m}^3$ ) for each air sample:

$$\mu\text{g} / \text{m}^3 = \frac{A}{AV}$$

Where:

$A_b$	=	Total ng Cr(VI) in blank
$A_s$	=	Total ng Cr(VI) in sample
$A$	=	ng Cr(VI) after blank correction
$[\text{ng/mL Cr(VI)}]_b$	=	Amount found (from calibration curve) in blank
$[\text{ng/mL Cr(VI)}]_s$	=	Amount found (from calibration curve) in sample
$(\text{Sol Vol})_b$	=	Blank solution volume (mL) from Section 3.5.5 (normally 10 mL*)
$(\text{Sol Vol})_s$	=	Sample solution volume (mL) from Section 3.5.5 (normally 10 mL*)
$AV$	=	Air volume (L)
$DF$	=	Dilution factor (if any, see Section 3.6.5)
	=	(mL Diluent + mL Aliquot)/mL Aliquot

\*The solution volume for each SPE sample is normally 25 mL.

3.7.4 For bulk samples, calculate the total composition (in %) of Cr(VI) in each sample using:

$$\%(w / w) \text{ Cr(VI)} = \frac{(A) (D) (100\%)}{(SW) (1000 \mu\text{g} / \text{mg})}$$

Where:

$A$	=	$\mu\text{g}$ Cr(VI) after blank correction
$D$	=	Dilution factor (if any)
$SW$	=	Aliquot (in mg) of bulk taken in Section 3.5.3

### 3.8 Reporting Results

- 3.8.1 For spray-paint samples, add results obtained from the SPE residue extraction, if any, to the initial extraction result.
- 3.8.2 Report air sample results to the industrial hygienist as  $\mu\text{g}/\text{m}^3$  Cr(VI).
- 3.8.3 Report wipe sample results to the industrial hygienist as total micrograms or milligrams.
- 3.8.4 Report bulk sample results to the industrial hygienist as approximate per cent Cr(VI).

## 4. Backup Data

This method has been validated using a full shift sample of 480-min taken at a flow rate of 2 L/min for a 960-L air volume. The method validation was conducted near the proposed OSHA TWA PEL of  $0.5 \mu\text{g}/\text{m}^3$  as Cr(VI). The sampling media used during the validation consisted of a two-section polystyrene cassette containing a 37-mm PVC filter and a cellulose backup pad. The 37-mm, 5- $\mu\text{m}$  pore size PVC filters were purchased from Mine Safety Appliances (MSA) (part no. 625413, Pittsburgh, PA) and from Omega Speciality Instrument Co. (cat. no. P-503700, Chelmsford, MA). The analytical method has been validated using soluble ( $\text{K}_2\text{Cr}_2\text{O}_7$ ) and insoluble ( $\text{PbCrO}_4$ ) chromate compounds.

The validation consisted of the following experiments and discussion:



- 1) An analysis of 18 spiked (soluble chromate) samples - This set consists of 6 samples each at 0.25×, 0.5×, and 1× the proposed OSHA TWA-PEL assuming 960-L air volumes, to determine bias, precision, and overall error (OE) (Note: One sample at 1× PEL was lost during analysis).
- 2) An analysis of 18 spiked (insoluble chromate) samples - This set consists of 6 samples each at 0.25×, 0.5×, and 1× the proposed OSHA TWA-PEL assuming 960-L air volumes, to determine bias, precision, and OE.
- 3) An evaluation of storage stability at room temperatures (20 to 25 °C) for 24 spiked samples.
- 4) A determination of the qualitative and quantitative detection limits for Cr(VI).
- 5) An interference study using varied amounts of reducing substances and addition of Mg (II) to prevent oxidation of Cr(III) to Cr(VI).
- 6) A comparison of BE dilutions using concentration ratios (v:v) of 1:10, 1:8, 1:5 and 1:2.
- 7) An analysis of 3 sets of Cr(VI) quality control (QC) samples.
- 8) An evaluation of a strong extraction solution for spray-paint samples.
- 9) An analysis of Cr(VI) field samples using both DPP and IC/UV-vis methods.
- 10) A summary.

An aerosol generation system to determine sampler efficiency was unavailable; however, this method (OSHA ID-215) uses the sampling device historically used for chromate collection, which was examined previously by NIOSH (5.13). All samples were analyzed using a Dionex model 4000, 4500i, or DX500 IC equipped with a postcolumn reagent delivery system and a UV-vis detector. A 100 µL sample loop was used on the Dionex 4000 and 4500i IC, and a 150 µL loop was used on the DX500 IC. The larger 150 µL sample loop on the DX500 increased the sensitivity slightly, allowing for the lower detection limits. All sample results were calculated from concentration-response curves and statistically examined for outliers. In addition, the analyses results were tested for homogeneity of variance. Possible outliers were determined using the Treatment of Outliers Test (5.21). Homogeneity of variance was determined using Bartlett's test (5.22). Statistical evaluation was conducted according to the Inorganic Methods Evaluation Protocol (5.23). The overall error (OE) (5.22) was calculated using the equation:

$$OE_i\% = \pm(|\text{bias}_i| + 2CV_i) \times 100\% \text{ (at the 95\% confidence level)}$$

Where *i* is the respective sample pool being examined.

#### 4.1 Spiked Sample Analysis

Samples were prepared by adding known amounts of K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub> and PbCrO<sub>4</sub> stock solutions to PVC filters (also see Section 4.2 for preparation) to determine bias, precision, and OE for the analytical portion of the method. Samples were prepared with and without the addition of phosphate buffer/Mg(II) to evaluate any difference in recoveries. The lower concentration, 0.25× and 0.5× TWA PEL were used for this comparison.

4.1.1 **Procedure:** The PVC filters were spiked using a 25-µL syringe (Hamilton Microliter/Gastight Syringe, Hamilton Co., Reno, NV). Spikes (both K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub> and PbCrO<sub>4</sub>) were 0.11, 0.20, and 0.40 µg as Cr(VI). These levels correspond approximately to 0.25, 0.5, and 1× the proposed OSHA TWA PEL for a 960-L air sample collected at a 2-L/min flow rate.

4.1.2 **Results:** Recoveries are presented in Tables 1a, 1b, and 1c. As shown, including addition of phosphate buffer/Mg(II) in Table 1c, the mean recovery for all levels tested is very close

to 1.0 for both soluble and insoluble chromate compounds. No DE corrections are necessary for Cr(VI) collection using PVC filters.

Table 1a  
Cr(VI) Analysis  
Analytical Recovery Using  $K_2Cr_2O_7$  Spikes

Level	N	Mean Recovery	SD	CV	OE <sub>T</sub> ±%
0.25 × PEL	6	1.047	0.061	0.058	16.3
0.5 × PEL	6	1.002	0.061	0.061	12.4
1 × PEL	5*	0.966	0.035	0.037	10.9
All Levels	17	1.007		0.054	11.5

\*One sample was lost in analysis.

Table 1b  
Cr(VI) Analysis  
Analytical Recovery Using  $PbCrO_4$  Spikes

Level	N	Mean Recovery	SD	CV	OE <sub>T</sub> ±%
0.25 × PEL	6	1.019	0.079	0.078	17.5
0.5 × PEL	6	0.970	0.021	0.021	7.2
1 × PEL	6	0.969	0.074	0.076	18.3
All Levels	18	0.986		0.064**	14.2

\*\* = CV<sub>1</sub> (pooled)

Table 1c  
Cr(VI) Analysis  
Analytical Recovery Using  $K_2Cr_2O_7$  Spikes  
After adding Phosphate Buffer/Mg(II)

Level	N	Mean Recovery	SD	CV	OE <sub>T</sub> ±%
0.25 × PEL	6	1.000	0.112	0.112	22.4
0.5 × PEL	7	0.985	0.007	0.008	3.1

Where

N = Number of Samples; SD = Standard Deviation  
CV = Coef. of Variation; OE<sub>T</sub> = Overall Error (Total)

#### 4.2. Storage Stability

Procedure: Twenty-four samples were spiked to evaluate stability prior to sample analysis. A  $PbCrO_4$  stock solution was used to spike samples near 0.5 × the proposed OSHA TWA PEL [as Cr(VI)] for a 960-L sample and to demonstrate stability for insoluble chromates. Data from the SLTC Quality Control Division indicates that spiked samples prepared using soluble potassium dichromate at concentrations specified in Section 1.4.7 were stable at least one month after spiking.

Solubility product values indicated that lead chromate was the least soluble of the chromate compounds commonly found in industry. However, data was not available for insoluble samples prepared in the extraction media. The  $PbCrO_4$  was weighed out, extracted into solution using BE and then spiked onto PVC filters. After spiking, all samples (sealed cassettes containing PVC filters) were stored under normal laboratory conditions (20 to 25°C) in a lab drawer. Six samples were initially extracted and analyzed, then six samples were extracted and analyzed after various periods of storage (5, 15, and 30 days).

Another storage experiment was also conducted using prepared extraction solutions with DBE and phosphate buffer/Mg(II). This experiment was performed separately to evaluate storage after the samples were prepared. Six samples were spiked using the soluble  $K_2Cr_2O_7$  stock solution at 0.25 × the proposed OSHA TWA PEL [as Cr(VI)] for a 960-L sample. These separate samples were initially extracted and analyzed, and then the same samples were analyzed after 30 days.

**Results:** As shown in Tables 2a and 2b, the results of both tests conducted at room temperature show the mean recovery from filter and extracted samples analyzed after 30 days was within  $\pm 5\%$  of the recovery value at Day 0.

Table 2a  
Storage Stability Using Insoluble  $\text{PbCrO}_4$   
0.5 $\times$  PEL

Day	N	Mean, $\mu\text{g}$	SD	CV	Recovery (%)
0	6	0.197	0.004	0.021	97.0
5	6	0.190	0.005	0.026	93.6
15	6	0.200	0.018	0.088	98.7
30	6	0.190	0.008	0.040	93.7

Table 2b  
Storage Stability Using Soluble  $\text{K}_2\text{Cr}_7\text{O}_4$  + DBE + Phosphate Buffer/Mg(II)  
0.25 $\times$  PEL

Day	N	Mean, $\mu\text{g}$	SD	CV	Recovery (%)
0	6	0.120	0.013	0.11	100
30	6	0.126	0.010	0.08	105

#### 4.3 Qualitative and Quantitative Detection Limit Study

A modification of the National Institute for Occupational Safety and Health (NIOSH) detection limit calculation procedure (5.24, 5.25) was used to calculate detection limits.

**Procedure:** Ten different concentrations were used by spiking six separate PBM/DBE solutions (Section 3.3.8) with aliquots of aqueous standards prepared from  $\text{K}_2\text{Cr}_2\text{O}_7$  (Section 3.3.11). All samples were analyzed using a 100- $\mu\text{L}$  sample injection loop and a UV-vis detector setting of 0.5 AUFS.

**Results:** The spiked sample results are shown in Table 3 for qualitative and quantitative detection limits, respectively. The qualitative detection limit was 1 ng [as Cr(VI)] when using a 10-mL solution volume. This corresponds to  $1.0 \times 10^{-3} \mu\text{g}/\text{m}^3$  as Cr(VI) for a 960-L air volume. The quantitative detection limit was 3 ng [as Cr(VI)] when using a 10-mL solution volume. This corresponds to  $3.0 \times 10^{-3} \mu\text{g}/\text{m}^3$  as Cr(VI) for an 960-L air volume.

Table 3  
Qualitative and Quantitative Detection Limits  
Cr(VI) Level (as ng/mL)

Sample Number	0.1 PA	0.2 PA	0.3 PA	0.4 PA	0.5 PA	0.6 PA	0.7 PA	0.8 PA	0.9 PA	1.0 PA
1	1644	4786	7292	11136	15252	17612	19970	23583	29116	31324
2	1726	4911	7264	11143	15772	17188	19978	23190	29956	31414
3	1774	4933	7319	11575	15510	17412	19725	23444	29348	31402
4	1742	4999	7486	11576	14859	16850	21384	23667	29237	31697
5	1436	4862	7017	11553	14530	17528	21658	23519	29289	30908
6	1748	4902	7039	11675	15404	16978	21638	23680	30207	31968

PA = Integrated Peak Area

The blank integrated peak areas and their standard deviations (std dev) were all equal to zero.

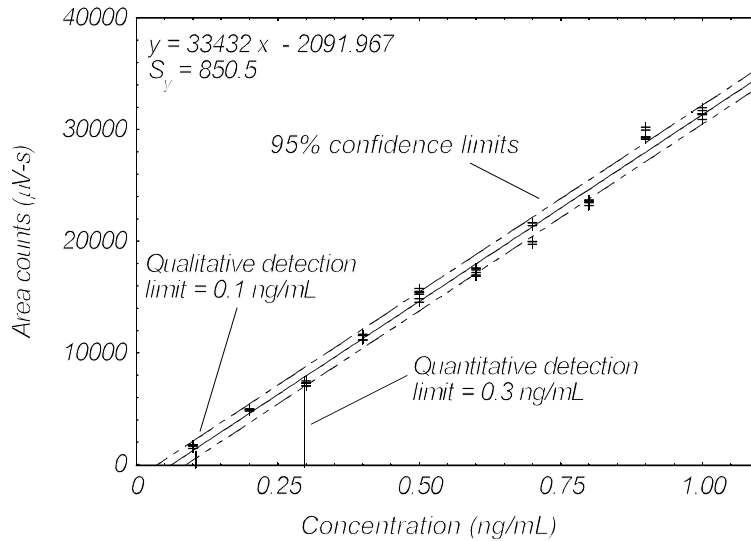


Figure 3. A plot of the standards to determine the detection limit.

The response of the low-level calibration samples were plotted to obtain the linear regression equation ( $Y = mX + b$ ), and the predicted responses ( $\hat{Y}_i$ ) at each  $X$ .

Using the equations:

$$S_y = [\sum(\hat{Y}_i - Y_i)^2 / (N - 2)]^{1/2}$$

$$Q1 = (3S_y) / m$$

$$Q2 = 3.33 Q1$$

Where:

- $Y_i$  = the measured response
- $m$  = analytical sensitivity or slope as calculated by linear regression
- $S_y$  = the standard error of the regression
- $N$  = the number of data points
- $Q1$  = qualitative detection limit
- $Q2$  = quantitative detection limit

Therefore,  $Q1 = (3S_y) / m$   
 $= 0.1 \text{ ng/mL as Cr(VI)}$   
 $\Rightarrow 1.0 \text{ ng as Cr(VI) (10-mL sample volume)}$   
 $\Rightarrow 1.0 \times 10^{-3} \mu\text{g/m}^3 \text{ as Cr(VI) (960-L air volume)}$

$Q2 = 3.33 Q1$   
 $\Rightarrow 3.0 \times 10^{-3} \mu\text{g/m}^3 \text{ as Cr(VI) (960-L air volume)}$

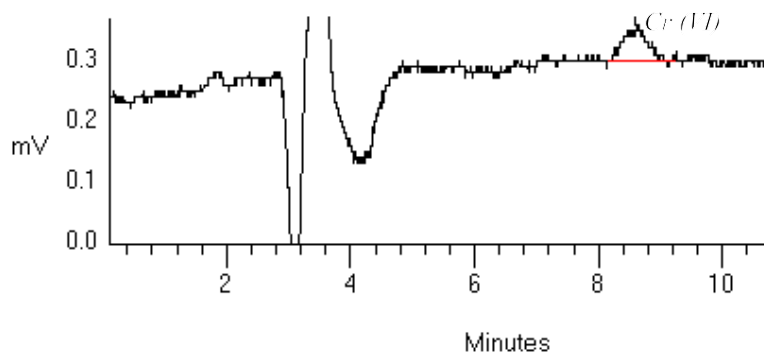


Figure 4. A chromatogram of the quantitative detection limit of 0.3 ng/mL Cr(VI).

It is interesting to note that the addition of phosphate buffer/Mg(II) to the solutions significantly increased detection limits. The qualitative and quantitative limits without addition of the Cr(III) conversion suppressor were approximately six times less than the limits stated above. In standards above 50 ng/mL this difference was not noted. In standards less than 50 ng/mL the difference between standards prepared with only BE and those with the addition of phosphate buffer/Mg(II) increases as the concentration of the standards decreases, such that the lower end of the calibration curve becomes quadratic.

#### 4.4 Interference Study

Six experiments to test potential interferences from various amounts of Cr(III), Fe(II), Fe(III), V(V), Mo(VI), Cu(I), and Mn(II) were conducted. These substances may coexist with Cr(VI) compounds in some workplace atmospheres and may also interfere with the analysis of Cr(VI) (5.3). The following chemicals were used for preparing the solution spikes for this study:

Potassium dichromate,  $K_2Cr_2O_7$ , for Cr(VI); Chromium nitrate,  $Cr(NO_3)_3 \cdot 9H_2O$ , for Cr(III); Ferrous sulfate,  $FeSO_4$ , for Fe(II); Ferric nitrate,  $Fe(NO_3)_3$ , for Fe(III); Vanadium pentoxide,  $V_2O_5$ , for V(V); Molybdenum trioxide,  $MoO_3$ , for Mo(VI); Cuprous chloride,  $Cu_2Cl_2$ , for Cu(I); Manganous chloride,  $MnCl_2 \cdot 4H_2O$ , for Mn(II); and Magnesium chloride,  $MgCl_2$ , or Magnesium sulfate,  $MgSO_4$ , for Mg(II).

All Cr(III) solutions were used to test how much, if any, Cr(III) converts to Cr(VI) on PVC filters or in solution. Mixtures using Mg(II) were used to determine its ability to suppress potential interferences. Early experiments were conducted using magnesium chloride to provide the magnesium needed to form the magnesium hydroxide precipitate with any Cr(III) present. Magnesium sulfate was also used in a comparison between the two salts in an extraction study. Both the chloride and the sulfate of magnesium gave comparable results. Magnesium sulfate is recommended in this method because of the better, larger precipitate formation. A significant difference between the two salts was not noted in terms of recovery, peak characteristics, or retention times. A difference was noted in that the magnesium chloride gave a precipitate that was more difficult to decant.

The six experiments are detailed in Sections 4.4.1 through 4.4.6 below.

4.4.1 Differing amounts of Cr(VI) and each of the interfering substances were mixed in the same volumetric flasks and then spiked onto individual PVC filters. The concentrations of the spikes varied from 0 to 10 times the Cr(VI) concentration.

Procedure: Fifteen different potential interference mixture combinations and six samples of each combination were prepared, extracted with BE, and analyzed after 1:1 dilution. A large amount (887.6 and 872 ng/mL) of Cr(VI) was used for the spikes in this Experiment (and also Experiment 3) so that any significant effect would be analytically obvious.

**Results:** The recoveries for Cr(VI) with varied amounts of reducing substances are shown in Table 4a.

Table 4a - Experiment 1  
Interference Study - 1:1 dilution BE  
Known Amount of Cr(VI) = 887.6 ng/mL

No.	Mixture Composition	Ratio	N	Mean, ng/mL	SD	CV	Recovery, % As Cr(VI)
1	Cr(VI) only	1:0	6	887.6	26.0	0.029	100
2	Cr(VI):Cr(III)	1:10	6	911.5	23.5	0.026	103
3	Cr(VI):Fe(II)	1:10	6	258.9	8.79	0.034	29.2
4	Cr(VI):Fe(III)	1:10	6	918.5	19.5	0.021	103
5	Cr(VI):V(V)	1:10	5	915.8	29.7	0.032	103
6	Cr(VI):Mo(VI)	1:10	6	874.5	16.6	0.019	98.5
7	Cr(VI):Cu(I)	1:10	6	898.0	76.4	0.085	101
8	Cr(VI):Mn(II)	1:10	6	838.0	33.9	0.040	94.4
9	Cr(VI):Fe(II)	1:1	6	811.1	18.1	0.022	91.4
10	Cr(VI):Fe(II)	1:5	6	643.8	12.5	0.019	72.5
11	Cr(VI):Cr(III):Fe(II)	1:1:1	6	848.5	17.5	0.021	95.6
12	Cr(VI):Cr(III):Fe(II)	1:5:5	6	566.3	15.9	0.028	63.8
13	Cr(VI):Cr(III):Fe(II)	1:10:10	6	291.5	10.0	0.034	32.8
14	Cr(VI):Cr(III):Fe(II): Fe(III):V(V):Mo(VI)	1:1:1: 1:1:1	6	841.5	11.8	0.014	94.8
15	Cr(VI):Cr(III):Fe(II): Fe(III):V(V):Mo(VI)	1:10:10: 10:10:10	6	761.6	30.8	0.040	85.8

As shown above, except for the solution containing large amounts of Fe(II) over Cr(VI), the recovery range is very close to 100%. When Cr(III) was added to Fe(II) and Cr(VI) the recovery is 91%, as shown in samples in set no. 9. Cr(III) added to 1:5 Cr(VI):Fe(II) had a recovery of 64%, as shown in samples in set no. 12. Cr(III) added to 1:10 Cr(VI):Fe(II) had recovery of 33%, as shown in samples in set no. 13. These losses occurred in a slightly acidic environment [both analytes were prepared in DI H<sub>2</sub>O (pH≈5.5) and contained in the same volumetric flask].

4.4.2 Once the Fe(II) interference was identified in Experiment 1, a smaller amount of Cr(VI) and Fe(II) were used for Experiment 2. An additional test was performed to determine conversion of Cr(III) to Cr(VI).

**Procedure:** Cr(VI) was spiked onto PVC filters first, dried, and then differing amounts of Fe(II) or Cr(III) were spiked on the Cr(VI) spot, dried, and then extracted with BE, and analyzed after 1:1 dilution.

**Results:** Table 4b shows the recoveries for Cr(VI) are close to 70% for 1:1, 1:5, and 1:10 Cr(VI) : Fe(II). This approximately 30% loss apparently occurred while both spikes were residing on the filter. A very small amount of Cr(III) converting to Cr(VI) is noted in Table 4b (0.71 ng/mL).

Table 4b - Experiment 2  
Interference Study - 1:1 dilution BE  
Known Amount of Cr(VI) =101.5 ng/mL

No.	Mixture Composition	Ratio or Amount	N	Mean, ng/mL	SD	CV	Recovery, % As Cr(VI)
1	Cr(VI) only	101.5 ng/mL Cr(VI)	6	101.5	3.72	0.037	100
2	Cr(III) only	1.0 µg/mL Cr(III)	6	0.71*	0.36	0.50	<1*
3	Cr(VI):Fe(II)	1:1	5	72.0	4.41	0.061	70.9
4	Cr(VI):Fe(II)	1:5	5	69.2	6.66	0.096	68.2
5	Cr(VI):Fe(II)	1:10	6	69.0	5.24	0.076	68.0

\*Cr(III) converted to Cr(VI)

4.4.3 The SPE solution, which contained 5% NaOH and 7.5% Na<sub>2</sub>CO<sub>3</sub>, was used as an extraction solution in Experiment 3 to evaluate the ease of converting Cr(III) to Cr(VI) in a stronger base. The experiment was also conducted to test whether or not magnesium (Mg) can prevent conversion of Cr(III) to Cr(VI) in SPE solutions. This conversion was noted in the literature (5.6) when using a NaOH/Na<sub>2</sub>CO<sub>3</sub> extraction similar to SPE, but was not noted in earlier work using BE solutions (5.8), primarily because of the significantly higher PEL and spiking concentrations used.

Procedure: Cr(VI) was spiked onto PVC filters first, dried, and then Cr(III) was spiked on the Cr(VI) spot, dried, and then extracted with SPE, and analyzed after 1:1 dilution.

Results: Table 4c shows adding 1 mg of Mg(II) can prevent Cr(III) converting to Cr(VI). This was the same conclusion presented in Reference 5.6.

Table 4c - Experiment 3  
Interference Study - 1:1 dilution SPE  
Known Amount of Cr(VI) =872 ng/mL

No.	Mixture Composition	Ratio or Amount	N	Mean, ng/mL	SD	CV	Cr(III) Converted to Cr(VI), %
1	Cr(VI) only	872 ng/mL Cr(VI)	4	872	16	0.018	-
2	Cr(III) only	10 µg/mL Cr(III)	4	18*	1.3	0.069	<0.2
3	Cr(VI):Cr(III)	1:10	4	880	12	0.013	<0.1
4	Cr(III) + 1 mg Mg(II)	10 µg/mL Cr(III)	4	ND	-	-	-
5	Cr(VI):Cr(III) + 1 mg Mg(II)	1:10	4	1055	10	0.012	<0.03

\*Cr(III) converted to Cr(VI)

Note: ND = 0.251 ng/mL as Cr(VI)

4.4.4 Experiment 4 was conducted to further test the effectiveness of Mg(II) with large proportions of Cr(III) to Cr(VI) in both BE and SPE solutions. Because Cr(VI) is significantly more toxic than Cr(III) [Note: The TWA PELs for Cr(VI) and Cr(III) are 0.50 µg/m<sup>3</sup> (proposed) and 1 mg/m<sup>3</sup>, respectively], the concentration ratio of Cr(VI) and Cr(III) in Experiment 4 was: Cr(VI) : Cr(III) = 250 ng: 5 mg = 1: 20,000.

Procedure: Experiment 4 included 10 tests. The first 5 tests were conducted using BE solution and the last 5 tests were conducted using SPE solution. Each sample was spiked with 250 ng of Cr(VI) or 5 mg of Cr(III) while contained in a 50-mL Erlenmeyer flask, 10 or 20 mg Mg(II), and then 5 mL BE (sample sets A through D) or SPE (sample sets A' through E') solution were added. Each sample was slowly extracted for 60 min, and finally diluted with DI H<sub>2</sub>O to the mark of a 10-mL volumetric flask for BE and 25 mL for SPE. The following are designated set numbers for Experiment 4 (Mg added as MgSO<sub>4</sub>):

- A: 250 ng of Cr(VI) (control samples);
- B: 5 mg of Cr(III) [check for conversion to Cr(VI) during extraction];
- C: 250 ng of Cr(VI) + 5 mg of Cr(III);
- D: C + 10 mg Mg(II);
- E: C + 20 mg Mg (II);
- A': 250 ng of Cr(VI) (control samples);
- B': 500 mg of Cr(III) [check for conversion to Cr(VI) during extraction];
- C': 250 ng of Cr(VI) + 5 mg of Cr(III);
- D': C' + 10 mg Mg(II);
- E': C' + 20 mg Mg(II);

Results: Table 4d data suggests that the oxidation of Cr(III) occurred during the alkaline extraction process. When alkalinity was increased by using 5% NaOH, more Cr(III) was oxidized to Cr(VI) (as shown in SPE, Samples A' to E'). Although the conversion is small as percentage of Cr(III), it is very significant in terms of the proposed PEL. A previous work conducted by the author (5.8) did not note the conversion in BE solutions; however, the larger detection limit and lack of significance (the PEL of 0.05 mg/m<sup>3</sup> was used in the past work) were contributing factors. The net conversion of Cr(III) to Cr(VI) is considered extremely minor when comparing amounts to the PEL of 0.05 mg/m<sup>3</sup>. In the presence of freshly precipitated magnesium hydroxide (10 or 20 mg of Mg) the oxidation of dissolved Cr(III) was suppressed to insignificantly low levels. As shown in Table 4d, the approach with Mg(II) is also applicable in the more strongly basic solution of SPE (5% NaOH/7.5% Na<sub>2</sub>CO<sub>3</sub>). It should be noted that the SPE extraction is performed after the BE extraction, and little, if any, soluble Cr(III) should still be present. It is important to note, for maximum effectiveness, the magnesium salt/phosphate buffer solution is added to the sample **before** BE or SPE solutions.

Table 4d - Experiment 4  
Interference Study - 1:1 dilution BE (A to D) and SPE (A' to E')  
Known Amount of Cr(VI) = 250 ng; Cr(III) = 5 mg

Set #	N	ng Cr(VI) found theoretical = 250 ng	SD	CV	Cr(III) converted to Cr(VI)(%)
A	6	249.57	3.98	0.016	-
B	6	128.03	7.93	0.062	0.00256
C	6	373.19*	7.74	0.021	0.00246
D	6	250.07*	5.27	0.021	-
E	6	237.82*	2.97	0.013	-
A'	6	253.06	3.60	0.014	-
B'	6	226.45	8.23	0.036	0.0045
C'	6	484.79*	13.07	0.027	0.0047
D'	6	281.43*	5.12	0.018	0.00063
E'	6	268.18*	6.17	0.023	0.00036

\*Cr(III) converted to Cr(VI) plus 250 ng Cr(VI) spike

4.4.5 Experiment 5 was conducted to repeat certain aspects of Experiment 4 and to determine the amount of Mg(II) needed to prevent Cr(III) conversion to Cr(VI) during the extraction process.

Procedure: Experiment 5 repeated the design of Experiment 4, except that Cr(VI) : Cr(III) = 500 ng:5 mg = 1:10,000. The following sets used in this experiment are (Mg(II) is as MgSO<sub>4</sub>):

- F: 500 ng of Cr(VI) + 5 mg of Cr(III) + 5 mg Mg(II) with BE;
- G: 500 ng of Cr(VI) + 5 mg of Cr(III) + 10 mg Mg(II) with BE;
- H: 500 ng of Cr(VI) + 5 mg of Cr(III) + 15 mg Mg(II) with BE;
- G': 500 ng of Cr(VI) + 5 mg of Cr(III) + 10 mg Mg(II) with SPE;

Results: Table 4e shows that, in BE solution, the addition of 5, 10, or 15 mg of Mg(II) to a mixture of Cr(III) and Cr(VI) gave comparable results. The slight decrease in recovery as Mg(II) increased



appears more so as noise resulting from analyzing a very small amount (500 ng) of Cr(VI). It was noted that the addition of Mg(II) produces a significant precipitate of magnesium hydroxide in the extraction solution and that the more added, the larger the precipitate. This precipitate must be carefully handled when transferring solutions for analysis to prevent injection into the ion chromatograph.

Table 4e - Experiment 5  
Interference Study - 1:1 dilution BE (F to H) and SPE (G')  
Known Amount of Cr(VI) = 500 ng; Cr(III) = 5 mg

Set #	N	Mean ng as Cr(VI) Theory=500ng	SD	CV	Cr(III) converted to Cr(VI), %
F	6	507.55*	2.88	0.0057	<0.01
G	6	496.59*	3.67	0.0074	-
H	6	497.35*	5.82	0.0096	-
G'	6	508.48*	4.86	0.0096	<0.01

\*Cr(III) converted to Cr(VI) plus 500 ng Cr(VI) spike.

4.4.6 Experiment 6 was performed to test whether or not adding Mg(II) or phosphate buffer (0.5 MKH<sub>2</sub>PO<sub>4</sub>/0.5 M K<sub>2</sub>HPO<sub>4</sub>)/Mg(II) can also prevent the negative Fe(II) interference on Cr(VI) analysis. The phosphate buffer is thought to aid in complexing the Cr(III) (5.5).

Procedure: Experiment 6 included 2 tests. The first test was conducted using only Mg(II) spiking on Fe(II); the second test was performed using the mixture of phosphate buffer/Mg(II) on the Fe(II). A known amount of Cr(VI) was spiked on one side of each PVC filter and the Fe(II) spiked on the other side of each filter. The filters were allowed to dry overnight and then Mg(II) or the mixture of phosphate buffer/Mg(II) was added prior to extraction with BE solution. The following sets were used for this experiment:

- I: 100 ng/mL of Cr(VI) + 1.0 µg/mL of Fe(II) + 10 mg Mg(II)(as MgCl<sub>2</sub>)
- J: 100 ng/mL of Cr(VI) + 1.0 µg/mL of Fe(II) + 10 mg Mg(II)(as MgCl<sub>2</sub> mixed with phosphate buffer).
- K: 100 ng/mL of Cr(VI) + 1.0 µg/mL of Fe(II) + 10 mg Mg(II) (as MgSO<sub>4</sub> mixed with phosphate buffer).

Results: Table 4f shows a significant increase in recovery of Cr(VI) as compared to Experiment 2 is noted when adding Mg(II) or phosphate buffer/Mg(II) mixture.

Table 4f - Experiment 6  
Interference Study - 1:1 dilution BE  
Known Amount of Cr(VI) = 100 ng/mL

Set #	Mixture Composition	Ratio	N	Mean, ng/mL	SD	CV	Recovery, % As Cr(VI)
I	Cr(VI):Fe(II)	1:10	6	92.7	4.29	0.046	92.7
J	Cr(VI):Fe(II)	1:10	6	96.6	3.41	0.035	96.6
K	Cr(VI):Fe(II)	1:10	6	95.8	1.59	0.026	95.8

#### 4.5 Comparison of Different DBE Solutions

Due to the strongly basic nature of the BE solution, a dilution with DI H<sub>2</sub>O needs to be performed prior to analysis. To determine the most effective dilution, the following experiment was performed.

Procedure: In order to compare the performance of this method and to potentially increase the analytical sensitivity, different DBE solutions were used for testing. Four DBE solutions were prepared from the original BE solution: 1) 1 to 10 dilution of original BE solution; 2) 1 to 8 dilution; 3) 1 to 5 dilution; and 4) 1 to 1 dilution. A spike of 80 ng/mL Cr(VI) was added to each dilution.

**Results:** Table 5 shows results of the comparison study. As shown, there were no significant differences among the recoveries, however; certain characteristics of the chromatogram changed as the concentration of BE changed.

Table 5  
Comparison Study - BE Dilution Factors

Dilution Factor 1 to x	N	Mean Cr(VI) µg	SD	CV	Ratio µg <sub>(1 to x)</sub> /µg <sub>(1 to 10)</sub>
1 to 10	6	77.5	3.6	0.047	-
1 to 8	6	80.6	1.7	0.021	1.04
1 to 5	6	76.5	2.9	0.037	0.99
1 to 1	5	77.3	3.5	0.046	1.00

An additional test was performed to assess the differences in the chromatogram using 100 ng/mL Cr(VI) standard in DI H<sub>2</sub>O, in a 1:1 dilution, and in BE. As shown in the following figure, a peak appearing just before the Cr(VI) peak becomes larger as the concentration of DBE solution becomes stronger, though the size of this peak also depends on the freshness of the DBE/PBM solution, the age of the standards or samples, and the back pressure of the pumps. Broadening of the Cr(VI) peak also occurs, indicating that matrix matching of the standards and samples is necessary. A dilution of 1:1 was chosen to maintain adequate sensitivity with minimal peak broadening when compared to aqueous standards.

#### 4.6 Evaluation of Extraction Solution for Spray-Paint Samples

**Procedure:** The resistance of spray-paints to extraction can be a serious problem as stated in OSHA method ID-103 (5.8). This method included a digestion step using perchloric and other mineral acids to assure all chromium was accounted for in spray-paint samples. In order to compare the extraction efficiency of solutions used for extracting Cr(VI) from spray-paint samples, two solutions were tested: 1) the buffer/extraction (BE) solution (10% Na<sub>2</sub>CO<sub>3</sub> / 2% NaHCO<sub>3</sub>); 2) a solution containing NaOH further designated as spray-paint extraction (SPE) (5% NaOH + 7.5% Na<sub>2</sub>CO<sub>3</sub>). Preparation of these two solutions are specified in Sections 3.3.3 and 3.3.4, respectively. Using a disposable plastic pipette, two drops of automotive finishes spray-paint (Sunfire 421, Acrylic

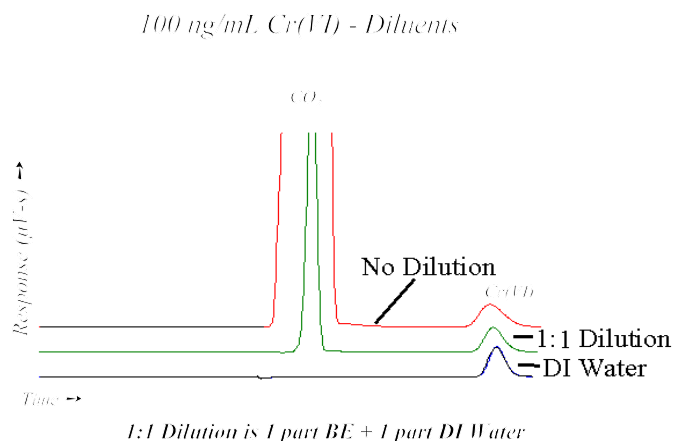


Figure 5. Overlapping chromatograms illustrating the effect of the amount of carbonate/magnesium/phosphate solution on these chromatograms.

Urethane Enamel, The Sherwin-William Co., Cleveland, OH) containing lead chromate (3% as chromium) were spiked onto PVC filters contained in individual 125-mL Phillips beakers. The

analyses followed the procedure described in Sections 3.5.1. through 3.5.7., however, due to the possible high content of Cr(VI), 5 mL of extraction solution (BE or SPE) was added to each sample, and then after extraction, diluted to 50 mL with DI H<sub>2</sub>O. One mL of this solution was then taken and diluted to 10 mL with DI H<sub>2</sub>O.

**Results:** Table 6 shows the results of a comparison of the effectiveness of these two extraction solutions. As shown, the SPE solution is superior to the BE solution for extraction of Cr(VI) in potentially resistant spray-paint samples.

Table 6  
Comparison Study - BE Solution vs. SPE Solution

Extraction Solution	N	Mean, µg	SD	CV	Ratio, SPE/BE
BE	5	142	9.9	0.069	-
SPE	5	211	33	0.16	1.49

#### 4.7 Comparison of Extraction with MgCl<sub>2</sub> and MgSO<sub>4</sub>

**Procedure:** PVC filters were spiked with 1 µg Cr(VI) and extracted with a solution of 10 mg/mL Mg (II), in the form of either MgCl<sub>2</sub> or MgSO<sub>4</sub>, in the phosphate buffer, and then BE solution was added.

**Results:** Table 7 shows that there was little difference in the extraction efficiency between the two different salts of magnesium.

Table 7  
Comparison Study - MgCl<sub>2</sub> vs MgSO<sub>4</sub>

Type of Mg	N	Mean ng Cr(VI)	SD	CV	Recovery, %
MgCl <sub>2</sub>	6	1000	2.31	.063	100
MgSO <sub>4</sub>	6	991	1.46	.042	99.1

#### 4.8. Analysis of Cr(VI) Quality Control (QC) Samples

**Procedure:** Three sets of Cr(VI) QC samples were prepared by an independent source by spiking 10 to 20 µg Cr(VI) on the PVC filters. Samples were analyzed using the conditions stated in Section 3 of this method.

**Results:** Table 8 shows the results of the QC samples, which have amounts typical of those near or over the PEL of 0.05 mg/m<sup>3</sup> Cr(VI). Samples with higher concentrations can be analyzed using this method provided higher standards are prepared to bracket the samples, or the appropriate aliquot/dilution is performed.

Table 8  
Cr(VI) QC Samples

Set	N	Mean, F/T*	SD	CV	Recovery, %
I	4	0.949	0.019	0.020	94.9
II	4	0.978	0.050	0.051	97.8
III	4	0.940	0.049	0.053	94.0
				0.044**	95.6 ave.

\*F/T = Found/Theoretical (Recovery)

\*\*CV (pooled)

#### 4.9 Analysis of Cr(VI) Field Samples

**Procedure:** In order to compare the new IC/UV-vis method to the previous method, Cr(VI) samples collected during field surveys were used. These samples had been previously analyzed by a SLTC chemist using the DPP method (OSHA method no. ID-103).

**Results:** Table 9 shows the Cr(VI) results in mg/m<sup>3</sup>. The DPP results are in parenthesis for comparison purposes. As shown, both methods are in good agreement except for a few very low concentrations in which the DPP method gave "none detected" results. However, for those DPP-ND samples, the IC/UV-vis method detected the presence of Cr(VI) and was able to quantitate amounts.

Table 9 - Analysis Cr(VI) Field Samples

Sample No.	Air Volume, L	ng/mL, Cr(VI)	µg, Cr(VI)	mg/m <sup>3</sup> , Cr(VI)
01	512.0	ND	ND	ND (ND)
02	632.0	ND	ND	ND (ND)
03	602.0	ND	ND	ND (ND)
04 (BI)	0	ND	ND	ND (ND)
05	42.5	62.9	6.29	0.1480 (0.1838)
06 (BI)	0	ND	ND	ND (ND)
07	876.0	8.98	2.25	0.0026 (0.0019)
08	588.0	6.81	1.70	0.0029 (0.0017)
09	802.0	9.82	2.46	0.0031 (0.0023)
10	0	ND	ND	ND (ND)
11	799.2	13.3	3.33	0.0042 (0.0039)
12	797.0	8.85	2.21	0.0028 (0.0020)
13	869.5	13.9	3.49	0.0040 (0.0041)
14	827.5	19.1	4.79	0.0058 (0.0059)
15	945.6	6.84	1.71	0.0018 (0.0011)
16	930.0	4.48	1.12	0.0013 (ND)
17	882.0	17.4	4.35	0.0049 (0.0050)
18	884.1	7.84	1.96	0.0022 (0.0016)
19	887.3	6.07	1.52	0.0017 (ND)
20	276.0	ND	ND	ND (ND)
21	392.0	5.37	1.34	0.0034 (ND)
22 (BI)	0	ND	ND	ND (ND)
23 (Wipe)	0	5.09	1.27 µg	1.27 µg (1.06 µg)
24	64.3	15.4	1.54	0.0239 (0.0247)
25	52.0	ND	ND	ND (ND)
26	181.7	ND	ND	ND (ND)
27 (Wipe)	0	6.00	1.50 µg	1.50 µg (0.85 µg)
28 (BI)	0	ND	ND	ND (ND)
29	63.0	4.72	0.47	0.0075 (ND)
30	74.1	ND	ND	ND (ND)
31 (BI)	0	ND	ND	ND (ND)
32	566.0	ND	ND	ND (ND)
33	658.0	ND	ND	ND (ND)

Note: For IC/UV-vis, ND=2.51 ng as Cr(VI). For DPP, ND=100 ng as Cr(VI) (5.6.). Both NDs are based on 10-mL solution volume.

#### 4.10. Summary

This analytical method has been shown to be precise and accurate when analyzing soluble and insoluble chromate compounds (as potassium dichromate and lead chromate, respectively) commonly found in the workplace. The validation results indicate the method meets the OSHA criteria for accuracy and precision (5.23). Performance during storage stability tests is adequate. Detection limits [as Cr(VI)] are very low when samples are taken for 8 h at 2 L/min. No significant interferences were found from various amounts of reducing substances except for samples containing Fe(II). Results indicate that not only does the addition of magnesium sulfate or

magnesium chloride prevent the conversion of Cr(III) to Cr(VI), but also can minimize the Fe(II) effect on Cr(VI) analysis.

A 1:1 dilution was used for optimal sensitivity. A peak prior to the Cr(VI) peak is noted, and slight peak broadening occurs with this dilution; however, as long as matrix matching of standards and samples occur, significant problems are not noted. The method demonstrates good performance in analyzing Cr(VI) QC samples and is not only in good agreement with the DPP technique (OSHA Method No. ID-103) when analyzing Cr(VI) field samples, but is more sensitive. A new spray-paint extraction solution was also developed for better extracting Cr(VI) from spray-paint samples.

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**APPENDIX C**

**NIOSH 7300 and Laboratory Modifications**

## Contract Analytical Lab Sample Preparation and Testing Details for Total Metals on 8" Glass Fiber Filters

**General Set Information:** This analytical batch consists of a single sample from work order 8079019 which was analyzed for chromium, copper, iron, lead, manganese, nickel and vanadium.

**Sample Preparation:** The 8-inch filter sample was cut into two halves (Section A and Section B) and each half was transferred to separate 250 ml beakers for digestion in the presence of 30 ml of concentrated nitric acid. Samples were initially heated on a hotplate for 30 minutes and then removed and allowed to cool. Another 20 ml of concentrated nitric acid were added to each sample and returned to the hotplate for an additional 30 minutes before removing and cooling. Aliquots of 6 ml of hydrogen peroxide and 4 ml of ASTM Type II water were then added to each of the samples, heated for 20 minutes on the hotplate, and removed. After cooling, 10 ml of concentrated hydrochloric acid and 10 ml of ASTM Type II water were then added to each sample. The samples were returned to the hotplate for two hours at ~96° C to reduce the volumes below 50 ml, then removed and allowed to cool. After cooling, the sample digestates were decanted to 100 ml volumetric flasks. A 40 ml aliquot of ASTM Type II water was then added to each of the beakers containing the extracted filters. After allowing the filters to soak for at least 30 minutes, the filter liquid was then decanted to the applicable 100 ml volumetric flasks containing the digestates. The filters, beaker walls, and watchglasses were then rinsed with additional aliquots of ASTM Type II water into the respective volumetric flasks and brought to 100 ml final volume. After shaking thoroughly, 50 ml portions of the digestates were then transferred into centrifuge tubes for subsequent analysis by ICP.

**Instrument Calibration:** Instrument calibration was performed in accordance with NIOSH method 7300.

**Initial and Continuing Calibration Verification Analysis:** The results for all initial calibration verification (ICV) and continuing calibration verification (CCV) samples are within the acceptance limits of +/- 10% of the respective target analyte concentrations.

**Initial and Continuing Calibration Blank Analysis:** The results for all initial and continuing calibration blanks were below the reporting limit for all target analytes.

**Reagent Blank Analysis:** The results for the reagent blank were below the reporting limit for all target analytes.



**Media Blank Analysis:** A media blank was prepared and analyzed with this sample.

The media blank consisted of a half-sheet of an 8"X10" glass fiber filter of the same composition as was used for collection of the field sample. The media blank was processed with the field sample through the entire digestion and analytical sequences. The results for all media blank were below the reporting limit for all target analytes.

**Laboratory Control Sample and Duplicate Analysis:** A Laboratory Control Sample (LCS) and a Laboratory Control Sample Duplicate (LCSD) were prepared and analyzed with this sample. These quality control samples were each prepared using a media blank consisting of a half-sheet of an 8"X10" glass fiber filter of the same composition as was used for collection of the field sample. Each of these media blanks were then spiked with 1 gram of an EPA reference soil containing the target analytes. These quality control samples were processed with the field sample through the entire digestion and analytical sequences. The control limits specified on the accompanying Quality Control Sample – Batch Report are not directly applicable to the quality control samples prepared for this analysis. The referenced control limits are specific to a 3.33 square inch strip of glass fiber filter using a variation of the sample preparation technique described above whereas these quality control samples were prepared on 40 square inches of glass fiber filter. It should also be noted that the field samples consisted of a total area of 50.26 square inches but that each sample filter was cut in half for the purposes of sample preparation (25.13 square inches).

**Replicate Analysis:** Replicate analysis was performed on the sample in this work order.

The results for the sample and its replicate were within the control limit of 20% RPD. If the result for the sample and/or its replicate is below the reporting limit, the 20% RPD control limit is not applicable.

**Dilution(s):** None

**Flagging Codes:** None

**Nonconformance/Corrective Action Report (NC/CAR):** None.

**Sample Calculation:** The results for each sample are calculated as follows:

Result for each sample section ( $\mu\text{g}/\text{sample}$ ) = (A) x (B) x (C)

Where:

A = Analyte concentration from instrument determination ( $\mu\text{g}/\text{L}$ )

B = Concentration factor from sample preparation  
=  $\frac{\text{Final Volume of Digestate (L)}}{\text{Sample section}}$

C = Dilution factor

Example Calculation:  $(1 \mu\text{g}/\text{L}) \times (0.2 \text{ L}/\text{sample}) \times (1) = 0.1 \mu\text{g}/\text{sample section}$

**Miscellaneous Comments:** Prior to analysis 4ml of Section A and Section B were mixed and used as the sample for analysis.

# ELEMENTS by ICP (Nitric/Perchloric Acid Ashing)

7300

MW: Table 1

CAS: Table 2

RTECS: Table 2

**METHOD:** 7300, Issue 3

**EVALUATION:** PARTIAL

**Issue 1:** 15 August 1990  
**Issue 3:** 15 March 2003

**OSHA:** Table 2  
**NIOSH:** Table 2  
**ACGIH:** Table 2

**PROPERTIES:** Table 1

<b>ELEMENTS:</b>	aluminum*	calcium	lanthanum	nickel	strontium	tungsten*
	antimony*	chromium*	lithium*	potassium	tellurium	vanadium*
	arsenic	cobalt*	magnesium	phosphorus	tin	yttrium
	barium	copper	manganese*	selenium	thallium	zinc
	beryllium*	iron	molybdenum*	silver	titanium	zirconium*
	cadmium	lead*				

\*Some compounds of these elements require special sample treatment.

SAMPLING		MEASUREMENT	
<b>SAMPLER:</b>	FILTER (0.8- $\mu$ m, cellulose ester membrane, or 5.0- $\mu$ m, polyvinyl chloride membrane)	<b>TECHNIQUE:</b>	INDUCTIVELY COUPLED ARGON PLASMA, ATOMIC EMISSION SPECTROSCOPY (ICP-AES)
<b>FLOWRATE:</b>	1 to 4 L/min	<b>ANALYTE:</b>	elements above
<b>VOL-MIN:</b>	Table 1	<b>ASHING</b>	
<b>-MAX:</b>	Table 1	<b>REAGENTS:</b>	conc. HNO <sub>3</sub> / conc. HClO <sub>4</sub> (4:1), 5 mL; 2mL increments added as needed
<b>SHIPMENT:</b>	routine	<b>CONDITIONS:</b>	room temperature, 30 min; 150 °C to near dryness
<b>SAMPLE</b>		<b>FINAL</b>	
<b>STABILITY:</b>	stable	<b>SOLUTION:</b>	4% HNO <sub>3</sub> , 1% HClO <sub>4</sub> , 25 mL
<b>BLANKS:</b>	2 to 10 field blanks per set	<b>WAVELENGTH:</b>	depends upon element; Table 3
<b>ACCURACY</b>		<b>BACKGROUND</b>	
		<b>CORRECTION:</b>	spectral wavelength shift
<b>RANGE STUDIED:</b>	not determined	<b>CALIBRATION:</b>	elements in 4% HNO <sub>3</sub> , 1% HClO <sub>4</sub>
<b>BIAS:</b>	not determined	<b>RANGE:</b>	varies with element [1]
<b>OVERALL PRECISION (<math>\hat{S}_{r,r}</math>):</b>	not determined	<b>ESTIMATED LOD:</b>	Tables 3 and 4
<b>ACCURACY:</b>	not determined	<b>PRECISION (<math>\hat{S}</math>):</b>	Tables 3 and 4

**APPLICABILITY:** The working range of this method is 0.005 to 2.0 mg/m<sup>3</sup> for each element in a 500-L air sample. This is simultaneous elemental analysis, not compound specific. Verify that the types of compounds in the samples are soluble with the ashing procedure selected.

**INTERFERENCES:** Spectral interferences are the primary interferences encountered in ICP-AES analysis. These are minimized by judicious wavelength selection, interelement correction factors and background correction [1-4].

**OTHER METHODS:** This issue updates issues 1 and 2 of Method 7300, which replaced P&CAM 351 [3] for trace elements. Flame atomic absorption spectroscopy (e.g., Methods 70XX) is an alternate analytical technique for many of these elements. Graphite furnace AAS (e.g., 7102 for Be, 7105 for Pb) is more sensitive.

**REAGENTS:**

1. Nitric acid (HNO<sub>3</sub>), conc., ultra pure.
2. Perchloric acid (HClO<sub>4</sub>), conc., ultra pure.\*
3. Ashing acid: 4:1 (v/v) HNO<sub>3</sub>:HClO<sub>4</sub>. Mix 4 volumes conc. HNO<sub>3</sub> with 1 volume conc. HClO<sub>4</sub>.
4. Calibration stock solutions, 1000 µg/mL. Commercially available, or prepared per instrument manufacturer's recommendation (see step 12).
5. Dilution acid, 4% HNO<sub>3</sub>, 1% HClO<sub>4</sub>. Add 50 mL ashing acid to 600 mL water; dilute to 1 L.
6. Argon.
7. Distilled, deionized water.

\* See SPECIAL PRECAUTIONS.

**EQUIPMENT:**

1. Sampler: cellulose ester membrane filter, 0.8-µm pore size; or polyvinyl chloride membrane, 5.0-µm pore size; 37-mm diameter, in cassette filter holder.
2. Personal sampling pump, 1 to 4 L/min, with flexible connecting tubing.
3. Inductively coupled plasma-atomic emission spectrometer, equipped as specified by the manufacturer for analysis of elements of interest.
4. Regulator, two-stage, for argon.
5. Beakers, Phillips, 125-mL, or Griffin, 50-mL, with watchglass covers.\*\*
6. Volumetric flasks, 10-, 25-, 100-mL, and 1-L\*\*
7. Assorted volumetric pipets as needed.\*\*
8. Hotplate, surface temperature 150 °C.

\*\* Clean all glassware with conc. nitric acid and rinse thoroughly in distilled water before use.

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**SPECIAL PRECAUTIONS:** All perchloric acid digestions are required to be done in a perchloric acid hood. When working with concentrated acids, wear protective clothing and gloves.

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**SAMPLING:**

1. Calibrate each personal sampling pump with a representative sampler in line.
2. Sample at an accurately known flow rate between 1 and 4 L/min for a total sample size of 200 to 2000 L (see Table 1) for TWA measurements. Do not exceed a filter loading of approximately 2 mg total dust.

**SAMPLE PREPARATION:**

3. Open the cassette filter holders and transfer the samples and blanks to clean beakers.
4. Add 5 mL ashing acid. Cover with a watchglass. Let stand 30 min at room temperature.  
NOTE: Start a reagent blank at this step.
5. Heat on hotplate (120 °C) until ca. 0.5 mL remains.  
NOTE 1: Recovery of lead from some paint matrices may require other digestion techniques. See Method 7082 (Lead by Flame AAS) for an alternative hotplate digestion procedure or Method 7302 for a microwave digestion procedure.  
NOTE 2: Some species of Al, Be, Co, Cr, Li, Mn, Mo, V, and Zr will not be completely solubilized by this procedure. Alternative solubilization techniques for most of these elements can be found elsewhere [5-10]. For example, aqua regia may be needed for Mn [6,12].
6. Add 2 mL ashing acid and repeat step 5. Repeat this step until the solution is clear.
7. Remove watchglass and rinse into the beaker with distilled water.
8. Increase the temperature to 150 °C and take the sample to near dryness (ca. 0.5 mL).
9. Dissolve the residue in 2 to 3 mL dilution acid.
10. Transfer the solutions quantitatively to 25-mL volumetric flasks.
11. Dilute to volume with dilution acid.  
NOTE: If more sensitivity is required, the final sample volume may be held to 10 mL.

**CALIBRATION AND QUALITY CONTROL:**

12. Calibrate the spectrometer according to the manufacturers recommendations.  
NOTE: Typically, an acid blank and 1.0 µg/mL multielement working standards are used. The following multielement combinations are chemically compatible in 4% HNO<sub>3</sub>/1% HClO<sub>4</sub>:
  - a. Al, As, Ba, Be, Ca, Cd, Co, Cr, Cu, Fe, La, In, Na
  - b. Ag, K, Li, Mg, Mn, Ni, P, Pb, Se, Sr, Tl, V, Y, Zn, Sc
  - c. Mo, Sb, Sn, Te, Ti, W, Zr
  - d. Acid blank
13. Analyze a standard for every ten samples.
14. Check recoveries with at least two spiked blank filters per ten samples.

**MEASUREMENT:**

15. Set spectrometer to conditions specified by manufacturer.
16. Analyze standards and samples.  
NOTE: If the values for the samples are above the range of the standards, dilute the solutions with dilution acid, reanalyze and apply the appropriate dilution factor in the calculations.

**CALCULATIONS:**

17. Obtain the solution concentrations for the sample, C<sub>s</sub> (µg/mL), and the average media blank, C<sub>b</sub> (µg/mL), from the instrument.
18. Using the solution volumes of sample, V<sub>s</sub> (mL), and media blank, V<sub>b</sub> (mL), calculate the concentration, C (mg/m<sup>3</sup>), of each element in the air volume sampled, V (L):

$$C = \frac{C_s V_s - C_b V_b}{V}, \text{mg} / \text{m}^3$$

NOTE: µg/L ≡ mg/m<sup>3</sup>

**EVALUATION OF METHOD:****Issues 1 and 2**

Method, 7300 was originally evaluated in 1981 [2,3]. The precision and recovery data were determined at 2.5 and 1000 µg of each element per sample on spiked filters. The measurements used for the method evaluation in Issues 1 and 2 were determined with a Jarrell-Ash Model 1160 Inductively Coupled Plasma Spectrometer operated according to manufacturer's instructions.

**Issue 3**

In this update of NIOSH Method 7300, the precision and recovery data were determined at approximately 3x and 10x the instrumental detection limits on commercially prepared spiked filters [12] using 25.0 mL as the final sample volume. Tables 3 and 4 list the precision and recovery data, instrumental detection limits, and analytical wavelengths for mixed cellulose ester (MCE) and polyvinyl chloride (PVC) filters. PVC Filters which can be used for total dust measurements and then digested for metals measurements were tested and found to give good results. The values in Tables 3 and 4 were determined with a Spectro Analytical Instruments Model End On Plasma (EOP)(axial) operated according to manufacturer's instructions.

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**METHOD REVISED BY:**

Mark Millson and Ronnee Andrews, NIOSH/DART.

Method originally written by Mark Millson, NIOSH/DART, and R. DeLon Hull, Ph.D., NIOSH/DSHEFS, James B. Perkins, David L. Wheeler, and Keith Nicholson, DataChem Laboratories, Salt Lake City, UT.

TABLE 1. PROPERTIES AND SAMPLING VOLUMES

Element (Symbol)	Properties		Air Volume, L @ OSHA PEL	
	Atomic Weight	MP, °C	MIN	MAX
Silver (Ag)	107.87	961	250	2000
Aluminum (Al)	26.98	660	5	100
Arsenic (As)	74.92	817	5	2000
Barium (Ba)	137.34	710	50	2000
Beryllium (Be)	9.01	1278	1250	2000
Calcium (Ca)	40.08	842	5	200
Cadmium (Cd)	112.40	321	13	2000
Cobalt (Co)	58.93	1495	25	2000
Chromium (Cr)	52.00	1890	5	1000
Copper (Cu)	63.54	1083	5	1000
Iron (Fe)	55.85	1535	5	100
Potassium (K)	39.10	63.65	5	1000
Lanthanum	138.91	920	5	1000
Lithium (Li)	6.94	179	100	2000
Magnesium (Mg)	24.31	651	5	67
Manganese (Mn)	54.94	1244	5	200
Molybdenum (Mo)	95.94	651	5	67
Nickel (Ni)	58.71	1453	5	1000
Phosphorus (P)	30.97	44	25	2000
Lead (Pb)	207.19	328	50	2000
Antimony (Sb)	121.75	630.5	50	2000
Selenium (Se)	78.96	217	13	2000
Tin (Sn)	118.69	231.9	5	1000
Strontium (Sr)	87.62	769	10	1000
Tellurium (Te)	127.60	450	25	2000
Titanium (Ti)	47.90	1675	5	100
Thallium (Tl)	204.37	304	25	2000
Vanadium (V)	50.94	1890	5	2000
Tungsten (W)	183.85	3410	5	1000
Yttrium (Y)	88.91	1495	5	1000
Zinc (Zn)	65.37	419	5	200
Zirconium (Zr)	91.22	1852	5	200

**TABLE 2. EXPOSURE LIMITS, CAS #, RTECS**

Element (Symbol)	CAS #	RTECS	Exposure Limits, mg/m <sup>3</sup> (Ca = carcinogen)		
			OSHA	NIOSH	ACGIH
Silver (Ag)	7440-22-4	VW3500000	0.01 (dust, fume, metal)	0.01 (metal, soluble)	0.1 (metal) 0.01 (soluble)
Aluminum (Al)	7429-90-5	BD0330000	15 (total dust) 5 (respirable)	10 (total dust) 5 (respirable fume) 2 (salts, alkyls)	10 (dust) 5 (powders, fume) 2 (salts, alkyls)
Arsenic (As)	7440-38-2	CG0525000	varies	C 0.002, Ca	0.01, Ca
Barium (Ba)	7440-39-3	CQ8370000	0.5	0.5	0.5
Beryllium (Be)	7440-41-7	DS1750000	0.002, C 0.005	0.0005, Ca	0.002, Ca
Calcium (Ca)	7440-70-2	--	varies	varies	varies
Cadmium (Cd)	7440-43-9	EU9800000	0.005	lowest feasible, Ca	0.01 (total), Ca 0.002 (respir.), Ca
Cobalt (Co)	7440-48-4	GF8750000	0.1	0.05 (dust, fume)	0.02 (dust, fume)
Chromium (Cr)	7440-47-3	GB4200000	0.5	0.5	0.5
Copper (Cu)	7440-50-8	GL5325000	1 (dust, mists) 0.1 (fume)	1 (dust) 0.1 (fume)	1 (dust, mists) 0.2 (fume)
Iron (Fe)	7439-89-6	NO4565500	10 (dust, fume)	5 (dust, fume)	5 (fume)
Potassium (K)	7440-09-7	TS6460000	--	--	--
Lanthanum	7439-91-0	--	--	--	--
Lithium (Li)	7439-93-2	--	--	--	--
Magnesium (Mg)	7439-95-4	OM2100000	15 (dust) as oxide 5 (respirable)	10 (fume) as oxide	10 (fume) as oxide
Manganese (Mn)	7439-96-5	OO9275000	C 5	1; STEL 3	5 (dust) 1; STEL 3 (fume)
Molybdenum (Mo)	7439-98-7	QA4680000	5 (soluble) 15 (total insoluble)	5 (soluble) 10 (insoluble)	5 (soluble) 10 (insoluble)
Nickel (Ni)	7440-02-0	QR5950000	1	0.015, Ca	0.1 (soluble) 1 (insoluble, metal)
Phosphorus (P)	7723-14-0	TH3500000	0.1	0.1	0.1
Lead (Pb)	7439-92-1	OF7525000	0.05	0.05	0.05
Antimony (Sb)	7440-36-0	CC4025000	0.5	0.5	0.5
Selenium (Se)	7782-49-2	VS7700000	0.2	0.2	0.2
Tin (Sn)	7440-31-5	XP7320000	2	2	2
Strontium (Sr)	7440-24-6	--	--	--	--
Tellurium (Te)	13494-80-9	WY2625000	0.1	0.1	0.1
Titanium (Ti)	7440-32-6	XR1700000	--	--	--
Thallium (Tl)	7440-28-0	XG3425000	0.1 (skin) (soluble)	0.1 (skin) (soluble)	0.1 (skin)
Vanadium (V)	7440-62-2	YW2400000	--	C 0.05	--
Tungsten	7440-33-7	--	5	5 10 (STEL)	5 10 (STEL)
Yttrium (Y)	7440-65-5	ZG2980000	1	N/A	1
Zinc (Zn)	7440-66-6	ZG8600000	--	--	--
Zirconium (Zr)	7440-67-7	ZH7070000	5	5, STEL 10	5, STEL 10



**TABLE 3. MEASUREMENT PROCEDURES AND DATA [1].  
Mixed Cellulose Ester Filters (0.45 µm)**

Element (a)	wavelength nm	Est. LOD µg/ Filter	LOD ng/mL	Certified 3x LOD (b)	% Recovery (c)	Percent RSD (N=25)	Certified 10x LOD (b)	% Recovery (c)	Percent RSD (N=25)
Ag	328	0.042	1.7	0.77	102.9	2.64	3.21	98.3	1.53
Al	167	0.115	4.6	1.54	105.4	11.5	6.40	101.5	1.98
As	189	0.140	5.6	3.08	94.9	2.28	12.9	93.9	1.30
Ba	455	0.005	0.2	0.31	101.8	1.72	1.29	97.7	0.69
Be	313	0.005	0.2	0.31	100.0	1.44	1.29	98.4	0.75
Ca	317	0.908	36.3	15.4	98.7	6.65	64.0	100.2	1.30
Cd	226	0.0075	0.3	0.31	99.8	1.99	1.29	97.5	0.88
Co	228	0.012	0.5	0.31	100.8	1.97	1.29	98.4	0.90
Cr	267	0.020	0.8	0.31	93.4	16.3	1.29	101.2	2.79
Cu	324	0.068	2.7	1.54	102.8	1.47	6.40	100.6	0.92
Fe	259	0.095	3.8	1.54	103.3	5.46	6.40	98.0	0.95
K	766	1.73	69.3	23.0	90.8	1.51	96.4	97.6	0.80
La	408	0.048	1.9	0.77	102.8	2.23	3.21	100.1	0.92
Li	670	0.010	0.4	0.31	110.0	1.91	1.29	97.7	0.81
Mg	279	0.098	3.9	1.54	101.1	8.35	6.40	98.0	1.53
Mn	257	0.005	0.2	0.31	101.0	1.77	1.29	94.7	0.73
Mo	202	0.020	0.8	0.31	105.3	2.47	1.29	98.6	1.09
Ni	231	0.020	0.8	0.31	109.6	3.54	1.29	101.2	1.38
P	178	0.092	3.7	1.54	84.4	6.19	6.40	82.5	4.75
Pb	168	0.062	2.5	1.54	109.4	2.41	6.40	101.7	0.88
<b>Sb</b>	206	0.192	7.7	3.08	90.2	11.4	12.9	<b>41.3</b>	32.58
Se	196	0.135	5.4	2.3	87.6	11.6	9.64	84.9	4.78
<b>Sn</b>	189	0.040	1.6	0.77	90.2	18.0	3.21	<b>49</b>	21.79
Sr	407	0.005	0.2	0.31	101.0	1.55	1.29	97.3	0.65
Te	214	0.078	3.1	1.54	102.0	2.67	6.40	97.4	1.24
Ti	334	0.050	2.0	0.77	98.4	2.04	3.21	93.4	1.08
Tl	190	0.092	3.7	1.54	100.9	2.48	6.40	99.1	0.80
V	292	0.028	1.1	0.77	103.2	1.92	3.21	98.3	0.84
<b>W</b>	207	0.075	3.0	1.54	<b>72.2</b>	10.1	6.40	<b>57.6</b>	14.72
Y	371	0.012	0.5	0.31	100.5	1.80	1.29	97.4	0.75
Zn	213	0.310	12.4	4.60	102.2	1.87	19.3	95.3	0.90
<b>Zr</b>	339	0.022	0.9	0.31	88.0	19.4	1.29	<b>25</b>	57.87

- (a) Bold values are qualitative only because of low recovery.  
(b) Values are certified by Inorganic Ventures INC. at 3x and 10x the approximate instrumental LOD  
(c) Values reported were obtained with a Spectro Analytical Instruments EOP ICP; performance may vary with instrument and should be independently verified.

**TABLE 4. MEASUREMENT PROCEDURES AND DATA [1].**  
**Polyvinyl Chloride Filter (5.0 µm)**

Element (c)	wavelength nm	Est. LOD µg per filter	LOD ng/mL	Certified 3x LOD (b)	% Recovery (a)	Percent RSD (N=25)	Certified <sup>17</sup> 10x LOD (b)	% Recovery (a)	Percent RSD (N=25)
Ag	328	0.042	1.7	0.78	104.2	8.20	3.18	81.8	18.9
Al	167	0.115	4.6	1.56	77.4	115.24	6.40	92.9	20.9
As	189	0.140	5.6	3.10	100.7	5.13	12.70	96.9	3.2
Ba	455	0.005	0.2	0.31	102.4	3.89	1.270	99.8	2.0
Be	313	0.005	0.2	0.31	106.8	3.53	1.270	102.8	2.1
<b>Ca</b>	317	0.908	36.3	15.6	<b>68.1</b>	12.66	64.00	96.8	5.3
Cd	226	0.0075	0.3	0.31	105.2	5.57	1.27	101.9	2.8
Co	228	0.012	0.5	0.31	109.3	4.67	1.27	102.8	2.8
Cr	267	0.020	0.8	0.31	109.4	5.31	1.27	103.4	4.1
Cu	324	0.068	2.7	1.56	104.9	5.18	6.40	101.8	2.4
Fe	259	0.095	3.8	1.56	88.7	46.82	6.40	99.1	9.7
K	766	1.73	69.3	23.4	96.4	4.70	95.00	99.2	2.2
<b>La</b>	408	0.048	1.9	0.78	<b>45.5</b>	4.19	3.18	98.8	2.6
Li	670	0.010	0.4	0.31	107.7	4.80	1.27	110.4	2.7
<b>Mg</b>	279	0.098	3.9	1.56	<b>54.8</b>	20.59	6.40	<b>64.5</b>	5.7
Mn	257	0.005	0.2	0.31	101.9	4.18	1.27	99.3	2.4
Mo	202	0.020	0.8	0.31	106.6	5.82	1.27	98.1	3.8
Ni	231	0.020	0.8	0.31	111.0	5.89	1.27	103.6	3.2
P	178	0.092	3.7	1.56	101.9	17.82	6.40	86.5	10.4
Pb	168	0.062	2.5	1.56	109.6	6.12	6.40	103.2	2.9
<b>Sb</b>	206	0.192	7.7	3.10	<b>64.6</b>	22.54	12.70	<b>38.1</b>	30.5
Se	196	0.135	5.4	2.30	83.1	26.23	9.50	76.0	17.2
<b>Sn</b>	189	0.040	1.6	0.78	85.7	27.29	3.18	<b>52.0</b>	29.4
<b>Sr</b>	407	0.005	0.2	0.31	<b>71.8</b>	4.09	1.27	81.2	2.7
Te	214	0.078	3.1	1.56	109.6	7.49	6.40	97.3	3.8
Ti	334	0.050	2.0	0.78	101.0	9.46	3.18	92.4	5.5
Tl	190	0.092	3.7	1.56	110.3	4.04	6.40	101.9	2.0
V	292	0.028	1.1	0.78	108.3	3.94	3.18	102.5	2.6
<b>W</b>	207	0.075	3.0	1.56	<b>74.9</b>	15.79	6.40	<b>44.7</b>	19.6
Y	371	0.012	0.5	0.31	101.5	3.63	1.27	101.4	2.5
Zn	213	0.310	12.4	4.70	91.0	68.69	19.1	101.0	9.6
<b>Zr</b>	339	0.022	0.9	0.31	<b>70.7</b>	54.20	1.27	<b>40.4</b>	42.1

- (a) Values reported were obtained with a Spectro Analytical Instruments EOP ICP; performance may vary with instrument and should be independently verified.
- (b) Values are certified by Inorganic Ventures INC. at 3x and 10x the approximate instrumental LOD [12].
- (c) Bold values are qualitative only because of low recovery. Other digestion techniques may be more appropriate for these elements and their compounds.

**APPENDIX D**

**Test Run Data Log**

### TEST RUN DATA LOG

Location:	
Date:	

Temperature:	
Relative Humidity:	

Capture Method	AWS Modified Fume Hood
Welding Process:	
Electrode Type/Size:	
Wire Density	gm/inch
Base Metal:	
Shielding Gas:	
Voltage:	
Current (amps):	
Arc Length:	
Travel Speed:	
Weld.Electrode Angle:	

**NOTES and OBSERVATIONS:**

#### Electrode Mass

Run #	Time		Inch/min Rod Initial	gm/inch Rod Final	Grams	Filter		Pres. Drop, in. water		CFM	
	Weld Time	Total Run*				Type	Lab ID	Start	Finish	Start	Finish
Blank											
1											
2											
3											
4											
5											
6											
7											
Blank											

\* Including time before weld start, weld time, and one minute after Welding Stop Time      Principal Investigator: \_\_\_\_\_

Welder: \_\_\_\_\_

Completed by: \_\_\_\_\_

**APPENDIX E**  
**NIOSH NMAM 0500**

# PARTICULATES NOT OTHERWISE REGULATED, TOTAL

0500

DEFINITION: total aerosol mass      CAS: NONE      RTECS: NONE

**METHOD:** 0500, Issue 2

**EVALUATION:** FULL

**Issue 1:** 15 February 1984  
**Issue 2:** 15 August 1994

**OSHA :** 15 mg/m<sup>3</sup>  
**NIOSH:** no REL  
**ACGIH:** 10 mg/m<sup>3</sup>, total dust less than 1% quartz

**PROPERTIES:** contains no asbestos and quartz less than 1%

**SYNONYMS:** nuisance dusts; particulates not otherwise classified

SAMPLING	MEASUREMENT
<p><b>SAMPLER:</b> FILTER (tared 37-mm, 5-µm PVC filter)</p> <p><b>FLOW RATE:</b> 1 to 2 L/min</p> <p><b>VOL-MIN:</b> 7 L @ 15 mg/m<sup>3</sup> <b>-MAX:</b> 133 L @ 15 mg/m<sup>3</sup></p> <p><b>SHIPMENT:</b> routine</p> <p><b>SAMPLE STABILITY:</b> indefinitely</p> <p><b>BLANKS:</b> 2 to 10 field blanks per set</p> <p><b>BULK SAMPLE:</b> none required</p>	<p><b>TECHNIQUE:</b> GRAVIMETRIC (FILTER WEIGHT)</p> <p><b>ANALYTE:</b> airborne particulate material</p> <p><b>BALANCE:</b> 0.001 mg sensitivity; use same balance before and after sample collection</p> <p><b>CALIBRATION:</b> National Institute of Standards and Technology Class S-1.1 weights or ASTM Class 1 weights</p> <p><b>RANGE:</b> 0.1 to 2 mg per sample</p> <p><b>ESTIMATED LOD:</b> 0.03 mg per sample</p> <p><b>PRECISION (<math>\hat{S}_r</math>):</b> 0.026 [2]</p>
ACCURACY	
<p><b>RANGE STUDIED:</b> 8 to 28 mg/m<sup>3</sup></p> <p><b>BIAS:</b> 0.01%</p> <p><b>OVERALL PRECISION (<math>\hat{S}_{rT}</math>):</b> 0.056 [1]</p> <p><b>ACCURACY:</b> ± 11.04%</p>	

**APPLICABILITY:** The working range is 1 to 20 mg/m<sup>3</sup> for a 100-L air sample. This method is nonspecific and determines the total dust concentration to which a worker is exposed. It may be applied, e.g., to gravimetric determination of fibrous glass [3] in addition to the other ACGIH particulates not otherwise regulated [4].

**INTERFERENCES:** Organic and volatile particulate matter may be removed by dry ashing [3].

**OTHER METHODS:** This method is similar to the criteria document method for fibrous glass [3] and Method 5000 for carbon black. This method replaces Method S349 [5]. Impingers and direct-reading instruments may be used to collect total dust samples, but these have limitations for personal sampling.

**EQUIPMENT:**

1. Sampler: 37-mm PVC, 2- to 5- $\mu$ m pore size membrane or equivalent hydrophobic filter and supporting pad in 37-mm cassette filter holder.
  2. Personal sampling pump, 1 to 2 L/min, with flexible connecting tubing.
  3. Microbalance, capable of weighing to 0.001 mg.
  4. Static neutralizer: e.g., Po-210; replace nine months after the production date.
  5. Forceps (preferably nylon).
  6. Environmental chamber or room for balance (e.g., 20 °C  $\pm$  1 °C and 50%  $\pm$  5% RH).
- 

**SPECIAL PRECAUTIONS:** None.

---

**PREPARATION OF FILTERS BEFORE SAMPLING:**

1. Equilibrate the filters in an environmentally controlled weighing area or chamber for at least 2 h.  
NOTE: An environmentally controlled chamber is desirable, but not required.
2. Number the backup pads with a ballpoint pen and place them, numbered side down, in filter cassette bottom sections.
3. Weigh the filters in an environmentally controlled area or chamber. Record the filter tare weight,  $W_1$  (mg).
  - a. Zero the balance before each weighing.
  - b. Handle the filter with forceps. Pass the filter over an antistatic radiation source. Repeat this step if filter does not release easily from the forceps or if filter attracts balance pan. Static electricity can cause erroneous weight readings.
4. Assemble the filter in the filter cassettes and close firmly so that leakage around the filter will not occur. Place a plug in each opening of the filter cassette. Place a cellulose shrink band around the filter cassette, allow to dry and mark with the same number as the backup pad.

**SAMPLING:**

5. Calibrate each personal sampling pump with a representative sampler in line.
6. Sample at 1 to 2 L/min for a total sample volume of 7 to 133 L. Do not exceed a total filter loading of approximately 2 mg total dust. Take two to four replicate samples for each batch of field samples for quality assurance on the sampling procedure.

**SAMPLE PREPARATION:**

7. Wipe dust from the external surface of the filter cassette with a moist paper towel to minimize contamination. Discard the paper towel.
8. Remove the top and bottom plugs from the filter cassette. Equilibrate for at least 2 h in the balance room.
9. Remove the cassette band, pry open the cassette, and remove the filter gently to avoid loss of dust.  
NOTE: If the filter adheres to the underside of the cassette top, very gently lift away by using the dull side of a scalpel blade. This must be done carefully or the filter will tear.

**CALIBRATION AND QUALITY CONTROL:**

10. Zero the microbalance before all weighings. Use the same microbalance for weighing filters before and after sample collection. Maintain and calibrate the balance with National Institute of Standards and Technology Class S-1.1 or ASTM Class 1 weights.

11. The set of replicate samples should be exposed to the same dust environment, either in a laboratory dust chamber [7] or in the field [8]. The quality control samples must be taken with the same equipment, procedures and personnel used in the routine field samples. The relative standard deviation calculated from these replicates should be recorded on control charts and action taken when the precision is out of control [7].

#### MEASUREMENT:

12. Weigh each filter, including field blanks. Record the post-sampling weight,  $W_2$  (mg). Record anything remarkable about a filter (e.g., overload, leakage, wet, torn, etc.)

#### CALCULATIONS:

13. Calculate the concentration of total particulate,  $C$  ( $\text{mg}/\text{m}^3$ ), in the air volume sampled,  $V$  (L):

$$C = \frac{(W_2 - W_1) - (B_2 - B_1) \cdot 10^3}{V}, \text{ mg}/\text{m}^3.$$

where:  $W_1$  = tare weight of filter before sampling (mg)  
 $W_2$  = post-sampling weight of sample-containing filter (mg)  
 $B_1$  = mean tare weight of blank filters (mg)  
 $B_2$  = mean post-sampling weight of blank filters (mg)

#### EVALUATION OF METHOD:

Lab testing with blank filters and generated atmospheres of carbon black was done at 8 to 28  $\text{mg}/\text{m}^3$  [2,6]. Precision and accuracy data are given on page 0500-1.

#### REFERENCES:

- [1] NIOSH Manual of Analytical Methods, 3rd ed., NMAM 5000, DHHS (NIOSH) Publication No. 84-100 (1984).  
 [2] Unpublished data from Non-textile Cotton Study, NIOSH/DRDS/EIB.  
 [3] NIOSH Criteria for a Recommended Standard ... Occupational Exposure to Fibrous Glass, U.S. Department of Health, Education, and Welfare, Publ. (NIOSH) 77-152, 119-142 (1977).  
 [4] 1993-1994 Threshold Limit Values and Biological Exposure Indices, Appendix D, ACGIH, Cincinnati, OH (1993).  
 [5] NIOSH Manual of Analytical Methods, 2nd ed., V. 3, S349, U.S. Department of Health, Education, and Welfare, Publ. (NIOSH) 77-157-C (1977).  
 [6] Documentation of the NIOSH Validation Tests, S262 and S349, U.S. Department of Health, Education, and Welfare, Publ. (NIOSH) 77-185 (1977).  
 [7] Bowman, J.D., D.L. Bartley, G.M. Breuer, L.J. Doemeny, and D.J. Murdock. Accuracy Criteria Recommended for the Certification of Gravimetric Coal Mine Dust Personal Samplers. NTIS Pub. No. PB 85-222446 (1984).  
 [8] Breslin, J.A., S.J. Page, and R.A. Jankowski. Precision of Personal Sampling of Respirable Dust in Coal Mines, U.S. Bureau of Mines Report of Investigations #8740 (1983).

#### METHOD REVISED BY:

Jerry Clere and Frank Hearl, P.E., NIOSH/DRDS.



**APPENDIX F**

**CORRESPONDENCE REGARDING POTENTIAL FOR SAMPLE LOSS ON  
CHAMBER WALLS**

**5/30/2013 E-mail from Robin Segall of U.S. Environmental Protection Agency to Joseph Jackens of Concurrent Technologies Corporation (CTC):**

Dear Joe,

I am writing to let you know that we have completed review of your shipyard welding test method for potential inclusion on our website as an Other Test Method (OTM). In general, the method looks very well thought out and we really appreciate the fact that you followed the specified format. However, in conducting our review, we discovered one issue requiring further exploration.

We would like to get additional background regarding the procedure described on page 15 of the method where the conical portion of the fume chamber is removed, blown out, and wiped clean before each new run. This procedure brings up the question as to whether there could be significant sample deposited on the walls of the chamber during welding that is not being captured on the filter during sampling and therefore not being analyzed. We are wondering if you conducted any experiments to determine the amount of PM/metals deposited on the conical portion of the fume chamber during welding or if you have any other engineering information that would address this issue?

This further investigation will not affect our work regarding the emissions factor information that you submitted.

Robin

Robin R. Segall  
Measurement Technology Group (E143-02)  
Office of Air Quality Planning & Standards  
US Environmental Protection Agency  
Research Triangle Park, NC 27711  
919-541-0893  
919-541-0615  
[segall.robin@epa.gov](mailto:segall.robin@epa.gov)

**8/8/2013 E-mail Response from Joseph Jackens of Concurrent Technologies Corporation (CTC) to Robin Segall of U.S. Environmental Protection Agency:**

Robin,

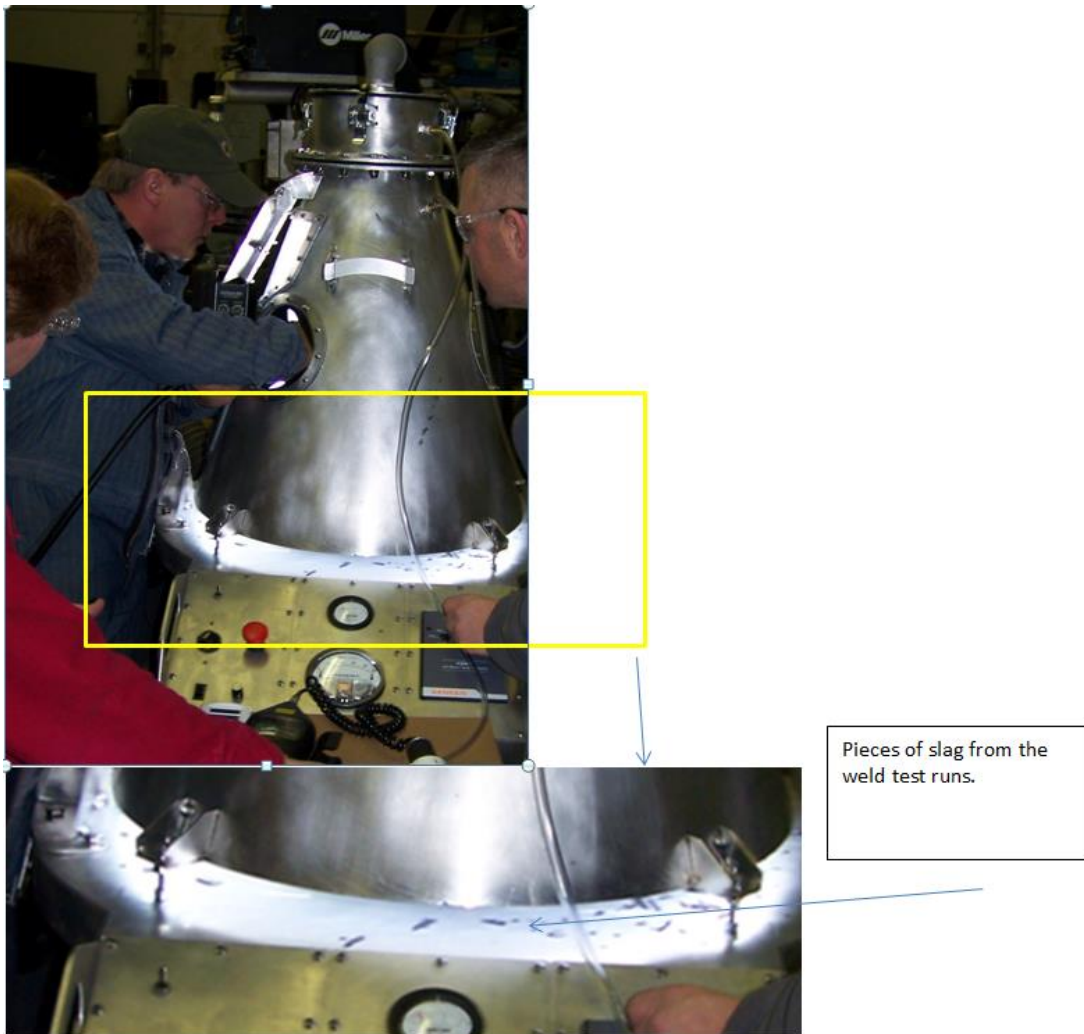
The NSRP Environmental Panel would like to thank you for coordinating this review. We have reviewed the comment that your group has provided, and have prepared a response to provide the clarification requested for the “blowing out and wiping out” of the chamber.

All testing was conducted in accordance with AWS F1.2:2006 “Laboratory Method for Measuring Fume Generation Rates and Total Fume Emission of Welding and Allied Processes”, published by the American Welding Society (AWS), and approved by the American National

Standards Institute (ANSI). This method was used as a basis for both building the chamber, and the procedures for sampling the weld emissions. The method does not warn against, nor does it mention anything regarding a risk of sample loss due to deposition on the chamber walls. This step was added due to observations in the field by the NSRP sampling team; specifically the team observed the build-up of large pieces of “slag”, which are chipped off the weld on the base metal. (This slag is depicted in Figures 1 and 2.) In short, the recommendation to “blow out and wipe out” the chamber between runs was added to ensure that the larger physical chunks of this slag were removed before the type of electrode or base metal was changed. This precautionary step eliminates the risk of slag from a test run, conducted with a specific electrode/base metal combination, from contaminating a new test run with a differing electrode/base metal combination. For example, if during the first run, several welding test were conducted with a stainless steel electrode, the slag may potentially contain a high percentage of Chromium. Before switching to a mild steel electrode for a second testing run, it was determined that removing the slag from the previous stainless steel run would eliminate the potential for carry over.



**Figure 1. Slag chipped off of welds on test plate.**



**Figure 2. Slag formed from test runs in weld fume chamber.**

In response to the specific question that you provided, “We are wondering if you conducted any experiments to determine the amount of PM/metals deposited on the conical portion of the fume chamber during welding or if you have any other engineering information that would address this issue?”:

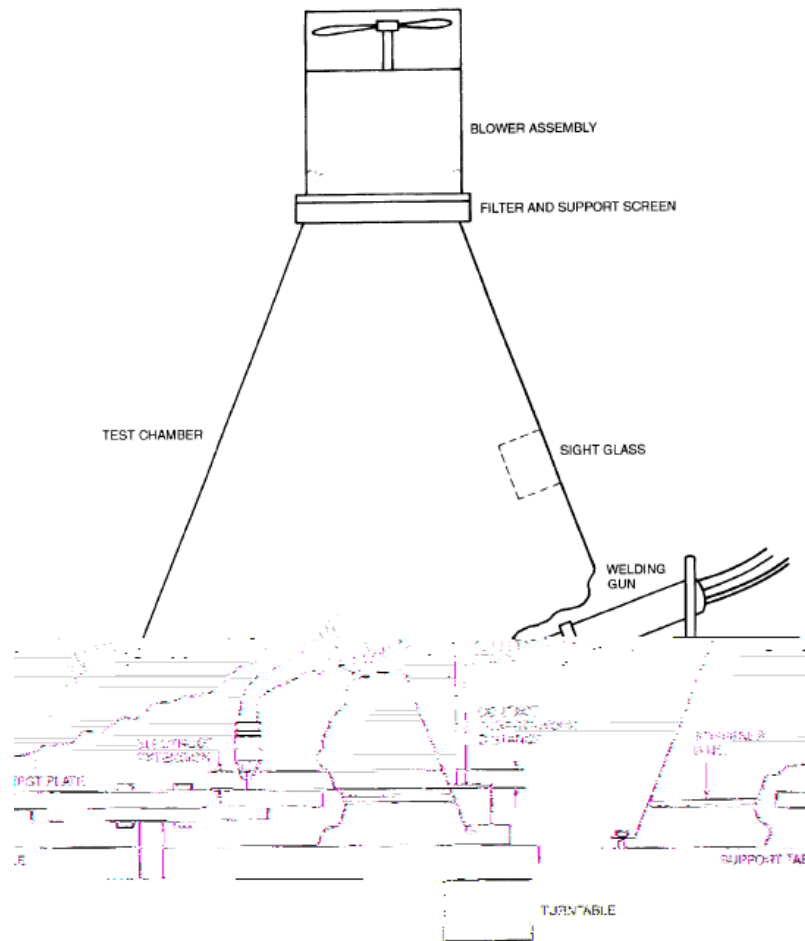
- No experiments were conducted to determine the amount of PM/metals deposited on the conical portion of the fume chamber during welding due to the following:
  - For fume capture, we adhered to the design and operating requirements for a conical test chamber described in AWS F1.2:2006 “Laboratory Method for Measuring Fume Generation Rates and Total Fume Emission of Welding and Allied Processes”, published by the AWS, and approved by ANSI. The method does not warn against, nor does it mention anything regarding a risk of sample loss, due to deposition on the walls. Relying on the expertise of the AWS, and the authority of ANSI, we did not identify a need to deviate from the standard nor conduct additional testing to confirm the fume capture method.

- The chamber design has been used in previous experiments to quantify weld fumes. Most relevant to the question regarding deposition is an article published in the peer reviewed journal, Journal of Air & Waste Management Association in 2007, entitled, “Emissions of Chromium (VI) from Arc Welding”, authored by William Heung, Myoung-Jin Yun, Daniel P.Y. Chang, and Peter G. Green from the Department of Civil and Environmental Engineering, University of California (UC), Davis, CA.
  - In their research, two methods of fume collection were used:
    - The AWS test method, which involved a rotating welding plate under a conical hood (consistent with the NSRP project).
    - A rectangular welding enclosure through which air was drawn to isokinetically capture total emissions on a bank of filters. The air from the welding operation was ducted into a 2-ft diameter circular hole that was cut into the wall above the welding surface. A conical transition was constructed to a 6-ft long, 4-in in diameter pipe that led to the bank of high-volume filters.
    - Comparison of Heung et al., (2007) results shows:
      - Both the AWS hood constructed by UC Davis, and the UC Davis enclosure were tested under the same welding conditions.
      - The AWS hood method provides published Fume Generation Rates (FGR), which were used as the baseline for comparison.
      - The resulting FGRs from the AWS hood and the enclosure were within 10% of the values reported in the AWS method; thus, both collection systems were deemed as accurate.
- Based on the fact the fume capture method was written by AWS and accepted by ANSI, we believed that it would produce comparable and scientifically defensible data. In addition, Heung et al., (2007), validated that the method can produce FGRs consistent with published calibration FGRs, and with FGRs developed from sampling conducted isokinetically; therefore, no additional sampling was conducted.
- In addition, prior to the testing, we participated in several meetings with U.S. EPA representatives, and coordinated reviews of the sampling and analysis plans with U.S. EPA subject matter experts. We received valuable input and technical comments, all of which were addressed and included in the test plan as appropriate; however, a request to investigate potential deposition of PM/metals using the AWS method was never received.

In regards to engineering information that would address this issue, we would like to reference two specific items: (1) the chamber design and fume capture; and, (2) reproducibility of results. Each is discussed below:

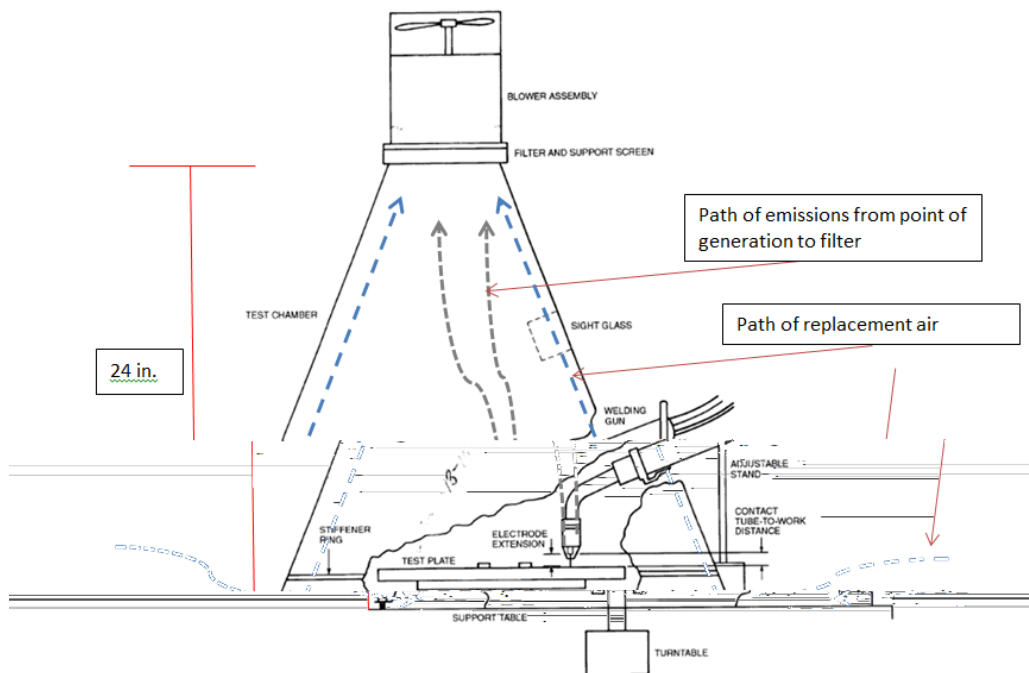
### 1. - Chamber Design and Fume Capture

The conical test chamber described in the method was developed in accordance with AWS F1.2:2006 “Laboratory Method for Measuring Fume Generation Rates and Total Fume Emission of Welding and Allied Processes”, published by the AWS, and approved by ANSI. The method provides schematics for a conical chamber, with a circular opening at the top (Figure 3).



**Figure 3. Cutaway View of the test chamber suggested by AWSF1.2:2006 (American Welding Society (AWS), 2006, p.4)**

The method requires an air pump, capable of sampling at a uniform rate of 25 to 35 ft<sup>3</sup>/min. The air inside the chamber is being pulled at a constant rate of no less than 25 ft<sup>3</sup>/min, prior to, during, and after welding has been conducted. The constant draw of air, at a minimum of 25 ft<sup>3</sup>/min, does not permit the emissions to gather, or collect in the chamber. Emissions are pulled vertically to the conical opening of the chamber, and through the filter. Replacement air is drawn in uniformly around the base of the chamber and travels up the inside walls of the chamber, therefore further directing any emissions that may potentially stray from the center of the chamber away from the wall, and towards the opening at the top. The projected air flows are depicted in Figure 4. The conical design along with the circular top reduces turbulence and eliminates any corners, which could potentially trap emissions, where they could potentially deposit.



**Figure 4. Cutaway View of the test chamber suggested by AWSF1.2:2006 (American Welding Society (AWS), 2006, p.4)**

## 2 – Reproducibility of Results

AWSF1.2:2006 states that, “This method describes a laboratory device and procedure for obtaining representative fume samples and determining fume generation rates of welding and allied processes”, and that the method “yields accurate and reproducible results”.

Through the various NSRP testing events, it has been shown that the AWS F.1.2:2006 chamber design yields reproducible results. The NSRP has executed 4 individual testing events, with several different electrodes, which resulted in a total of 20 test series involving various base metal and electrode combinations. When evaluating the integrity and comparability of the data from these test series, it was found that the standard deviation of all 20 tests series was relatively low, < 2.714, with the majority, 17 test series, less than 2.000. A low standard deviation indicates that the data points tend to be very close to the mean. It is anticipated that if deposition was occurring it would not be uniform from run to run, and that a greater data spread would have been observed and thus, a larger standard deviation would have been observed as well.