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HEXAVALENT CHROMIUM IN WORKPLACE ATMOSPHERES

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): Action Level (AL):	 0.50 µg/m^3 0.25 µg/m^3
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_2CO_3)/ 2% sodium bicarbonate ($NaHCO_3$) 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: Quantitative:	 1.0×10^{-3} µg/m^3 as Cr(VI) (960-L air sample) 3.0×10^{-3} µg/m^3 as Cr(VI) (960-L air sample)
Precision and Accuracy (Soluble and Insoluble) Validation Range: CV_1(pooled): Bias: Overall Error:	 0.12 to 0.42 µg/m^3 (960-L air sample) 0.059 - 0.004 ±12.9%
Method Classification:	Validated Method
Chemists:	James C. Ku, Mary Eide
Date:	June, 1998

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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 ($MCrO_4$), such as lead chromate, or also as chromium trioxide (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-µm 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% Na_2CO_3 and 2% $NaHCO_3$ 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 µg/m^3 for the Time Weighted Average (TWA) and 0.25 µg/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 Zatka 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 (Na_2CO_3), 2% sodium bicarbonate ($NaHCO_3$), and the phosphate buffer/magnesium sulfate mixture. The reaction between any chromate species and carbonate is illustrated by the following equation (5.3):

$$MCrO_4 + CO_3^{2-} \longrightarrow MCO_3 + CrO_4^{2-}$$

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.

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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_2CO_3 extraction solution with the mixture of phosphate buffer/Mg(II) (see Section 3.5.7). Using a well-buffered ammonium sulfate [$(NH_4)_2SO_4$] and ammonium hydroxide (NH_4OH) eluent, Cr(VI) is chromatographed as the yellow divalent CrO_4^{2-} 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

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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^3 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 1.0×10^{-3} µg/m^3 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 3.0×10^{-3} µg/m^3 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 2.47×10^4 area units per 1 ng/mL, when using a Dionex Series 4500i ion chromatograph with AI450 computer software (Dionex, Sunnyvale, CA). The sensitivity was 1.57×10^4 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_1), bias, and total overall error (OE) are as follows:

For soluble chromate:
CV_1 (pooled) = 0.054; bias = + 0.007; OE_T = ±11.5%

For insoluble chromate:
CV_1 (pooled) = 0.064; bias = - 0.014; OE_T = ±14.2%

For both types of chromate compounds (pooled soluble and insoluble):
CV_1 (pooled) = 0.059; bias = - 0.004; OE_T = ±12.9%

1.4.6 The collection efficiency of 0.945 ± 0.035 has been previous 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:

	Method Used	
	DPP*	IC/UV-vis
Samples (N):	282	57
Average recovery:	94.1%	94.8%
CV_1(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.

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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)

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	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 tetraoxychromate; 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_3	K_2CrO_4	$PbCrO_4$	$ZnCrO_4$*	$K_2Cr_2O_7$
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 alkalies.	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 $4ZnO{\cdot}CrO_3{\cdot}3H_2O$, 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 $\mu g/m^3$) 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

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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.)

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.

2.1 Equipment

2.1.1 Calibrated personal sampling pumps capable of sampling within ±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-µm 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).

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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^2. 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

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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-µm pore size (part no. SLSR 025 NS, Millipore Corp., Bedford, MA).

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.

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.

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3.3.1 Principal reagents:

Sodium carbonate (Na_2CO_3), 99%
Sodium bicarbonate ($NaHCO_3$), 99%
Potassium dichromate ($K_2Cr_2O_7$), 99.9% or Potassium chromate (K_2CrO_4), 99.9%
Magnesium sulfate, anhydrous ($MgSO_4$), 99%
Ammonium sulfate [$(NH_4)_2SO_4$], 99+%
Ammonium hydroxide (NH_4OH), 29%
1,5-Diphenylcarbazide (DPC) - $C_6H_5NHNHCONHNHC_6H_5$, 99%
Methanol (CH_3OH), HPLC grade
Sulfuric acid (H_2SO_4), concentrated (98%)
Nitric acid (HNO_3), concentrated (69 - 71%)
Deionized water (DI H_2O)

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 HNO_3 to about 500-mL DI H_2O contained in a 1.0-L volumetric flask and dilute to the mark with DI H_2O.

3.3.3 Buffer/extraction (BE) solution (10% Na_2CO_3 + 2% $NaHCO_3$):

Dissolve 100 g Na_2CO_3 and 20 g $NaHCO_3$ in about 500 mL DI H_2O 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 H_2O. 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% NaOH + 7.5% Na_2CO_3):

Dissolve 50 g NaOH and 75 g Na_2CO_3 in about 500 mL DI H_2O 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 H_2O. 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 [~10 mg/mL as Mg(II)]:

Dissolve 9.90 g of anhydrous $MgSO_4$ in 100-mL volumetric flask containing 50 mL DI H_2O. Mix well and dilute to the mark with DI H_2O. Prepare monthly.

3.3.6 Phosphate buffer (0.5 M KH_2PO_4/0.5 M $K_2HPO_4 \cdot 3H_2O$):

Dissolve 6.80 g of KH_2PO_4 and 11.41 g of $K_2HPO_4 \cdot 3H_2O$ in 100-mL volumetric flask containing 50 mL DI H_2O. Mix well and dilute to the mark with DI H_2O. Prepare monthly.

3.3.7 Phosphate buffer/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 H_2O). Prepare just before each analysis.

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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_2O. 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 $(NH_4)_2SO_4$ + 100 mM NH_4OH]:

Dissolve 33 g of $(NH_4)_2SO_4$ in about 500 mL of DI H_2O. Add 6.5 mL of 29% NH_4OH. Mix well and dilute with DI H_2O 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_3OH + 1N H_2SO_4):

1) First dissolve 0.5 g of DPC in 100 mL of HPLC grade CH_3OH. 2) Add 28 mL of 98% H_2SO_4 to about 500 mL of DI H_2O (**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_2O. 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 $K_2Cr_2O_7$ or 0.3735 g of K_2CrO_4 to 1.0 L with DI H_2O. 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_2O. Prepare these solutions weekly. Alternately, volumetric pipets and 10-mL volumetric flasks may be used to prepare standards through serial dilutions.

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_2CrO_4 or $K_2Cr_2O_7$). 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.

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):

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Working Std (ng/mL)	Std Solution (µg/mL)	Aliquot (µL)	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% HNO_3, and DI H_2O (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°C is adequate for extraction. If the hotplate cannot be adjusted to 135°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.

Note: Always add PBM solution before adding the extraction solution. 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).

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 °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 Cr(VI) to 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 H_2O. Dilute to volume with DI H_2O.

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 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).

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_2O. 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:

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.

Ion Chromatograph

Eluent:	250 mM $(NH_4)_2SO_4$ /100 mM NH_4OH
Postcolumn reagent:	2 mM DPC/10% CH_3OH/1 N H_2SO_4
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

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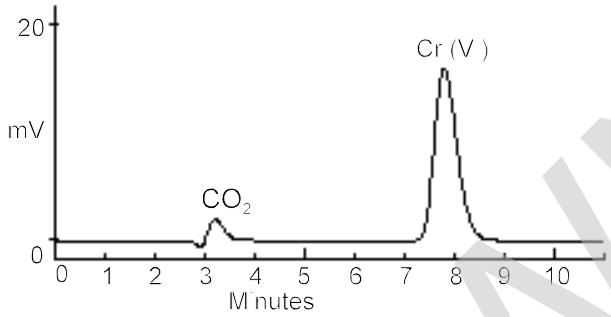
Postcolumn reagent flow rate: ~0.34 mL/min

Chromatogram:



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

The CO_2 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_2 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.)

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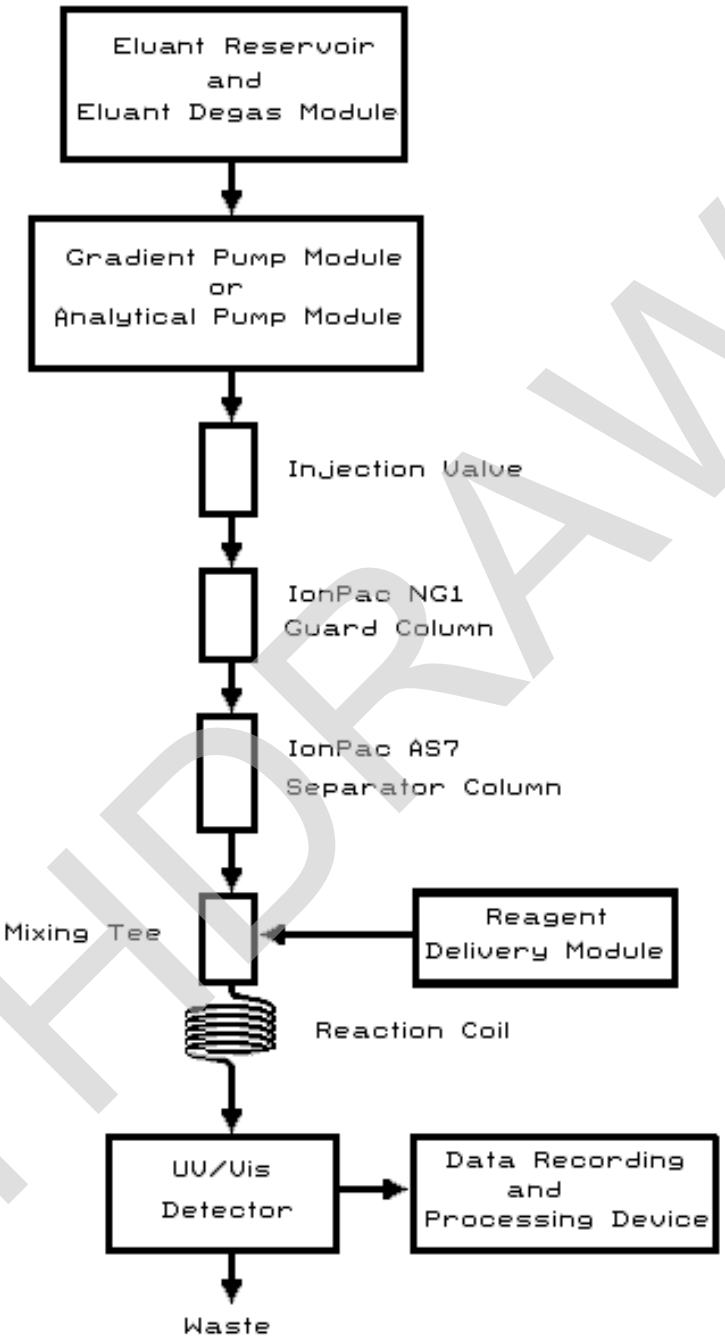

Figure 1. A diagram of the system flow path.

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

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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

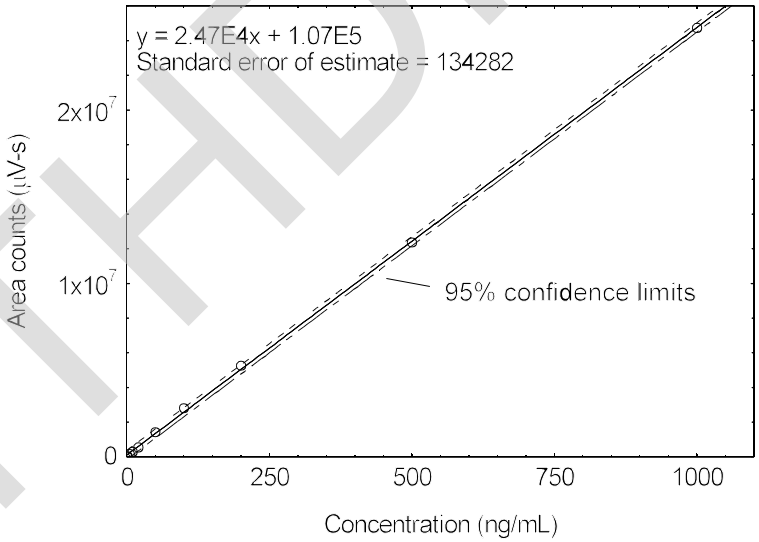

Figure 2. A plot of the standard curve of the above standards.

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.

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

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

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

Then calculate the air concentration of Cr(VI) (in µg/m^3) for each air sample:

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

Where:

A_b	=	Total ng Cr(VI) in blank
A_s	=	Total ng Cr(VI) in sample
A	=	ng Cr(VI) after blank correction
$[ng/mL\ Cr(VI)]_b$	=	Amount found (from calibration curve) in blank
$[ng/mL\ Cr(VI)]_s$	=	Amount found (from calibration curve) in sample
$(Sol\ Vol)_b$	=	Blank solution volume (mL) from Section 3.5.5 (normally 10 mL*)
$(Sol\ Vol)_s$	=	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:

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

Where:

A	= µg 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 µg/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 µg/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-µm 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 ($K_2Cr_2O_7$) and insoluble ($PbCrO_4$) chromate compounds.

The validation consisted of the following experiments and discussion:

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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:

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

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

4.1 Spiked Sample Analysis

Samples were prepared by adding known amounts of $K_2Cr_2O_7$ and $PbCrO_4$ 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 $K_2Cr_2O_7$ and $PbCrO_4$) 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

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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_T ±%
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_T ±%
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_1 (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_T ±%
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 Derivation
CV = Coef. of Variation; OE_T = 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.

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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 ±5% of the recovery value at Day 0.

Table 2a
Storage Stability Using Insoluble $PbCrO_4$
0.5× PEL

Day	N	Mean, µg	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 $K_2Cr_7O_4$ + DBE + Phosphate Buffer/Mg(II)
0.25× PEL

Day	N	Mean, µg	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 $K_2Cr_2O_7$ (Section 3.3.11). All samples were analyzed using a 100-µL 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 1.0×10^{-3} µg/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 3.0×10^{-3} µg/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.

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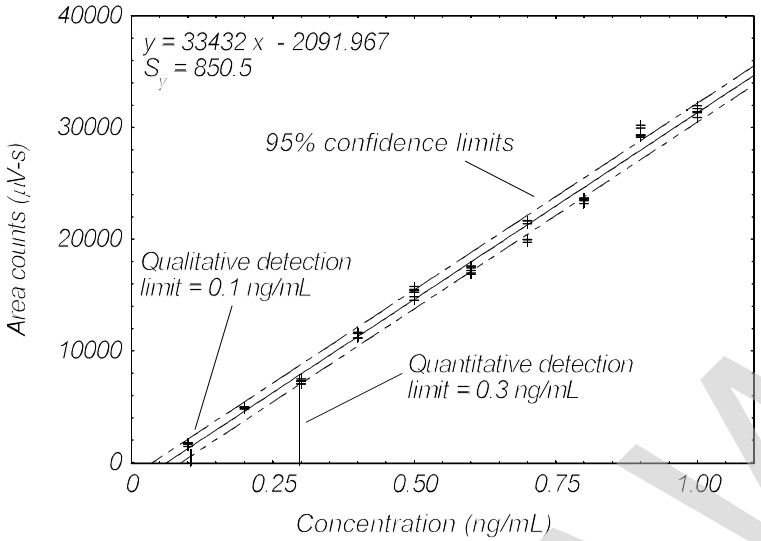

Figure 3. A plot of the standards to determine the detection limit.

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:

$$S_y = [\sum(\hat{Y}_i - Y_i)^2/(N - 2)]^{½}$$
$$Q1 = (3S_y)/m$$
$$Q2 = 3.33\ Q1$$

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 ng/mL as Cr(VI)
⇒ 1.0 ng as Cr(VI) (10-mL sample volume)
⇒ 1.0×10^{-3} µg/m^3 as Cr(VI) (960-L air volume)

$Q2 = 3.33\ Q1$
⇒ 3.0×10^{-3} µg/m^3 as Cr(VI) (960-L air volume)

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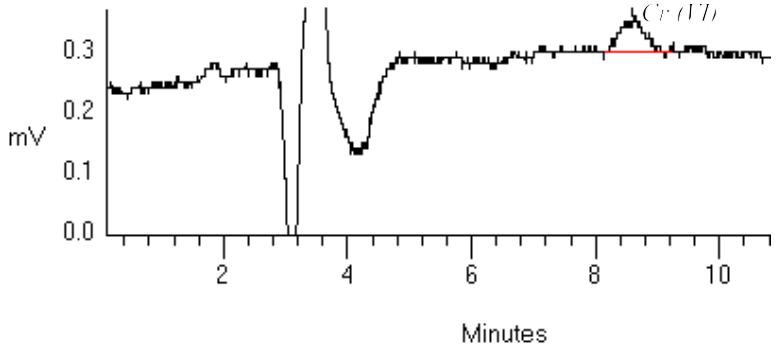

Figure 4. A chromatogram of the quantitative detection limit of 0.3 ng/mL Cr(VI).

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.

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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_2O (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).

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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_2CO_3, 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_2CO_3 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^3 (proposed) and 1 mg/m^3, 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_2O 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 $MgSO_4$.):

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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^3 was used in the past work) were contributing factors. The net conversion of Cr(III) to Cr(IV) is considered extremely minor when comparing amounts to the PEL of 0.05 mg/m^3. 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_2CO_3). 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 $MgSO_4$):

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(IV) gave comparable results. The slight decrease in recovery as Mg(II) increased

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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 M KH_2PO_4/0.5 M K_2HPO_4)/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 $MgCl_2$)
J: 100 ng/mL of Cr(VI) + 1.0 µg/mL of Fe(II) + 10 mg Mg(II)(as $MgCl_2$ mixed with phosphate buffer).
K: 100 ng/mL of Cr(VI) + 1.0 µg/mL of Fe(II) + 10 mg Mg(II) (as $MgSO_4$ 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_2O 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.

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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 $\mu g_{(1 \text{ to } x)}/\mu g_{(1 \text{ to } 10)}$
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_2O, 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_2CO_3 / 2% $NaHCO_3$); 2) a solution containing NaOH further designated as spray-paint extraction (SPE) (5% NaOH + 7.5% Na_2CO_3). 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

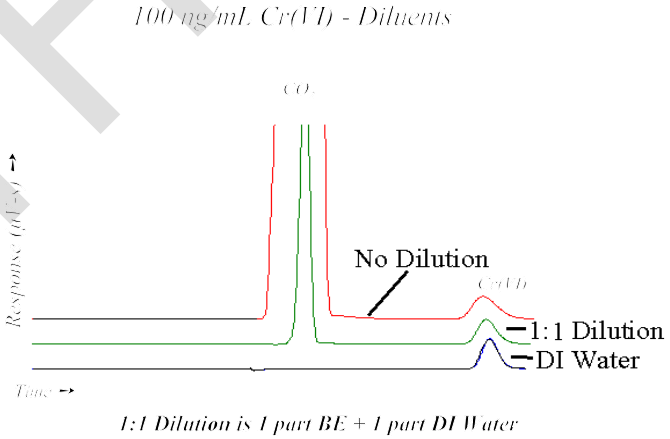

Figure 5. Overlapping chromatograms illustrating the effect of the amount of carbonate/magnesium/phosphate solution on these chromatograms.

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

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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_2O. One mL of this solution was then taken and diluted to 10 mL with DI H_2O.

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 $MgCl_2$ and $MgSO_4$

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 $MgCl_2$ or $MgSO_4$, 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 - $MgCl_2$ vs $MgSO_4$

Type of Mg	N	Mean ng Cr(VI)	SD	CV	Recovery, %
$MgCl_2$	6	1000	2.31	.063	100
$MgSO_4$	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^3 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).

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Results: Table 9 shows the Cr(VI) results in mg/m^3. 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^3, Cr(VI)
01	512.0	ND	ND	ND (ND)
02	632.0	ND	ND	ND (ND)
03	602.0	ND	ND	ND (ND)
04 (Bl)	0	ND	ND	ND (ND)
05	42.5	62.9	6.29	0.1480 (0.1838)
06 (Bl)	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 (Bl)	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 (Bl)	0	ND	ND	ND (ND)
29	63.0	4.72	0.47	0.0075 (ND)
30	74.1	ND	ND	ND (ND)
31 (Bl)	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

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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.

5. References

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Note: OSHA no longer uses or supports this method (December 2019).

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