Method no: ID-215 (version 2)
Control no.: T-ID215-FV-02-0604-M

Target concentration: 1.0 µg/m^3
OSHA PEL: 5.0 µg/ m^3 hexavalent chromium (Cr (VI)) (General Industry, Shipyards, and Construction) (Published 2/28/06) See hexavalent chromium standard for compliance dates and special provisions (71 FR 10100-10385 or 29 CFR 1910.1026; 29 CFR 1915.1026; 29 CFR 1926.1126)
ACGIH TLV: 0.05 mg/m^3 (50 µg/m^3) (water-soluble Cr (VI) compounds)
0.01 mg/m^3 (10 µg/m^3) (insoluble Cr (VI) compounds)

Procedure: Chromium plating operations are sampled by drawing known volumes of air through 37-mm polystyrene cassettes containing NaOH coated binderless quartz fiber filters (NaOHqz). Alternatively, PVC filters with cellulose back-up pads (BUP) in polystyrene cassettes can be used to sample chromium plating operations but these samples require special treatment after receipt at the analytical laboratory.

All other chromium operations are sampled by drawing known volumes of air through 37-mm or 25-mm polystyrene cassettes containing PVC filters with BUP.

The filters are extracted with hot 10% Na_2CO_3/2% $NaHCO_3$ (BE) and phosphate buffer/magnesium sulfate (PBM) solutions (BE/PBM). The interior walls of sampling cassettes are wiped with a PVC filter wetted with a solution of 50% BE, 15% PBM, and 35% water (DBE) and are analyzed separately. Samples from paint operations require a second extraction with hot 5% NaOH/7.5% Na_2CO_3 (SPE) and PBM solutions (SPE/PBM) following BE/PBM extraction. After dilution, the samples are analyzed by ion chromatography with UV-vis detection at 540-nm following post-column derivatization with 1,5-diphenyl carbazide.

Recommended sampling time and sampling rate: 480 min at 2.0 L/min (960 L)

	NaOHqz	PVC using BE/PBM	PVC using SPE/PBM
Reliable quanitation limit:	3.2 ng/m^3	3.5 ng/m^3	2.9 ng/m^3
SEE:	5.1%	5.2%	5.2%

Special requirements: Cr (VI) samples collected on PVC filters must be shipped overnight to OSHA Salt Lake Technical Center (SLTC) within 24 hours of sampling.
Cr (VI) samples collected on PVC filters from welding operations must be analyzed within 8 days of sampling (Section 4.5.6).
Cr (VI) samples from chromium plating operations collected on PVC filters must either be analyzed within 6 days of sampling or be stabilized as described in Section 1.

Status of method: Validated method. This method has been subjected to the established evaluation procedures of the Methods Development Team. For the sake of brevity, certain evaluation data reported in the first version of ID-215 was not included in version 2. That data remains available in the first version.

September 1998
Revised April 2006

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1. General Discussion

For assistance with accessibility problems in using figures and illustrations presented in this method, please contact Salt Lake Technical Center (SLTC) at (801) 233-4900. These procedures were designed and tested for internal use by OSHA personnel. Mention of any company name or commercial product does not constitute endorsement by OSHA.

1.1 Background

1.1.1 History

OSHA ID-103[1] was OSHA's previous method for hexavalent chromium (Cr (VI)) and it employed 37-mm polyvinyl chloride (PVC) filters for air sampling, sample extraction with carbonate/bicarbonate buffer solution, and analysis by differential pulse polarography. OSHA ID-103 was not sensitive enough to monitor the lower levels proposed in OSHA's Cr (VI) rulemaking[2]. Therefore, a new method (OSHA ID-215[3]) was developed that also utilized PVC filters and carbonate/bicarbonate extraction, but used a more sensitive and specific analytical technique. The technique in ID-215 was ion chromatography with post column derivatization and UV detection. The purpose of the carbonate/bicarbonate buffer solution extraction is to convert both soluble and insoluble chromium-containing chemicals to soluble carbonate compounds thereby allowing both chromium forms to be extracted. OSHA ID-215 also differs from OSHA ID-103 by use of magnesium sulfate/phosphate buffer[4] to precipitate potential metal interferences, mainly Fe (II) and Cr (III).

OSHA ID-215 (version 2) includes new data from tests of analytical procedures intended to extend the method to adequately address more Cr (VI) commercial operations than did the original version of OSHA ID-215. Results from these tests show that:

> As has been found in studies of other particulates[5], significant amounts of Cr (VI) are often deposited on the interior walls of sampling cassettes (Section 4.8.6). Tests showed that Cr (VI) equivalent to 0 to 123% of the amounts found on the PVC filter were present on the interior walls of cassettes used for compliance samples. It is now routine procedure to wipe interior walls of sampling cassettes for all metal samples analyzed at SLTC.
>
> Welding samples must be analyzed within eight days after sampling (Section 4.9.2). Storage stability tests showed that these samples were not stable for longer periods of time. Storage stability studies of PVC filters spiked with Fe (II) and Cr (VI), to mimic welding samples, showed that the interaction between Fe (II) and Cr (VI) to form Cr (III) continues after the sample is collected. The loss exceeded 10% after 7 days, showing that the samples should be shipped by overnight delivery service to the analytical laboratory within 24 hours of sampling, and that they must be analyzed within 8 days of collection (Section 4.9.2).

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[1] Ku, J., Hexavalent Chromium ID-103, http://www.osha.gov/dts/sltc/methods/inorganic/id103/id103.html (accessed 11/2/04).

[2] Safety and Health Topics Hexavalent Chromium, http://www.osha.gov/SLTC/hexavalentchromium/index.html (accessed 11/2/05).

[3] Eide, M., Ku, J., Hexavalent Chromium ID-215, http://www.osha.gov/dts/sltc/methods/inorganic/id215/id215.html (accessed 11/2/05).

[4] Vitale, R.J., Mussoline, G.R., Petura, J.C., James, B.R., Hexavalent Chromium Extraction from Soils. *J. Environ. Qual.* **1994,** *Vol. 23,* 1249-1256.

[5] Puskar, M.A., Harkins, J.M., Moomey, J.D., Hecker, L.H., Internal Wall Losses of Pharmacectical Dusts During Closed-Face, 37-mm Polystyrene Cassette Sampling. *Am.Ind. Hyg. Assoc. J.* **July 1991**, *Vol. 52*, 280-286.

Chromium plating samples collected on PVC filters must either be analyzed within 6 days of sampling or be stabilized immediately upon arrival at the analytical laboratory. Samples are stabilized by removing the filters from the cassettes and placing them in labeled glass vials each containing 5 mL of BE. Acids from chromium plating operations are neutralized by BE solution, and stabilization allows samples to be stored for up to two weeks before analysis (Section 4.5.3). The interior walls of sampling cassettes should be wiped with a PVC filter that has been wetted with 1 drop of dilute BE/PBM, and then also stabilized by placing it into separate labeled vials containing 5 mL of BE.

NaOHqz is a convenient alternative sampling medium for chromium plating samples. They showed excellent storage stability and required no special treatment after sampling (Section 4.5.1). Other interference studies have shown that NaOHqz can not be used to sample Cr (VI) in other work operations due to the interaction between NaOH and the interferences that may be present.[6]

Spray-paint samples are extracted with hot BE/PBM followed by a second extraction with hot SPE/PBM (Section 4.9.2). A second, more alkaline extraction is necessary to complete the extraction of insoluble Cr (VI) bound in the paint matrix.[7] Insoluble forms of Cr (VI) are not soluble in water but are soluble in warm basic solutions. The two extractions, BE/PBM followed by SPE/PBM, were necessary to break down the matrix of the paint to release the Cr (VI) present and get it dissolved (Section 4.9.2).

NIOSH Method 7600 for Cr (VI) recommends sampling with a 37-mm polystyrene cassette containing a PVC filter and a BUP.[8] The NIOSH method requires separating the filter from the BUP within an hour after sampling to prevent Cr (VI) from reacting with the BUP. The PVC filter is placed in a scintillation vial for shipment to the analytical laboratory and the BUP is discarded. Retention and storage stability studies conducted at SLTC using $K_2Cr_2O_7$ spiked PVC samples with BUPs, which had 960 liters of 80% RH air drawn through at 2 L/min, showed no migration of Cr (VI) from the filter to the BUP, and no interaction between Cr (VI) on the filter and the BUP after 15 days of storage (Section 4.5.2). Therefore, OSHA ID-215 (version 2) does not require separation of the PVC filter from the BUP for sample shipment.

Both soluble and insoluble forms of hexavalent chromium were used in the tests using PVC filters. The tests using NaOHqz filters used only soluble Cr (VI), as that was the only form present in chromium plating operations. Soluble Cr (VI) is defined as Cr (VI) from $K_2Cr_2O_7$ dissolved in DI water; and insoluble Cr (VI) as Cr (VI) from $PbCrO_4$ dissolved in BE solution. While $PbCrO_4$ is insoluble in water, it is readily soluble in warm BE solution.

1.1.2 Toxic effects (This section is for information only and should not be taken as the basis of OSHA policy.)[9]

The main health effects of workplace exposure to Cr (VI) are lung cancer, asthma, bronchitis, and damage to nasal epithelia, skin, and eyes. The U.S. Public Health Service studied the morbidity and mortality of male workers in seven U.S. chromate manufacturing plants during 1940-1950 and found 29 times as many deaths from

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[6] Eide, M., A Study of the Iron (II) Interference in Samples Requesting Analysis for Hexavalent Chromium, 2002, unpublished.

[7] Molina, D., Abell, M.T., An Ion Chromatographic Method for Insoluble Chromates in Paint Aerosol. *Am. Ind. Hyg. Assoc. J.* **1987***, Vol.48*, 830-335.

[8] NIOSH Method 7600 Chromium, Hexavalent. www.cdc.gov/niosh/nmam/pdfs/7600.pdf (accessed 11/2/05).

[9] Safety and Health Topics: Hexavalent Chromium. http://www.osha.gov/SLTC/hexavalentchromium/index.html (accessed 11/5/05).

respiratory cancer (excluding the larynx) when compared to the mortality rates for the total U.S. population. Studies of workers exposed to chromates in other countries have also shown a significant increase in lung cancer deaths.

1.1.3 Workplace exposure[10,11]

Cr(VI) compounds (which include: chromium trioxide, chromates and dichromates such as salts of sodium, potassium, ammonium, calcium, barium, zinc, strontium, and lead) have been widely used in the chemical industry in pigments, metal plating, and chemical synthesis as ingredients and catalysts. Chromates are used as high quality pigments for textile dyes, paints, inks, glass, and plastics. Cr(VI) can be produced during welding operations even if the chromium was originally present in another valence state. Historical uses such as an oxidizing agent in leather tanning have been replaced by other chemicals.

1.1.4 Physical properties and other descriptive information

(physical properties listed below are for common salts of Cr (VI) and do not represent all compounds containing Cr (VI))

IMIS number (all compounds containing Cr (VI))[12]: 0689
IMIS number used prior to 5/30/2006 (Chromic acid and Chromates (as CrO_3))[13]: 0686

chromium trioxide[14]

synonyms:	chromic acid; chromic anhydride; chromia; chromic trioxide		
CAS number:	1333-82-0	appearance:	dark purple-red crystals
molecular weight:	99.99	melting point:	197 °C
chemical formula:	CrO_3	solubility:	very sol in water, insol in alcohol

lead chromate[15]

synonyms:	chromic acid, lead salt; Crocoite; Phoenicochroite; plumbous chromate		
CAS number:	7758-97-6	appearance:	yellow crystals
molecular weight:	323.20	melting point:	844 °C
chemical formula:	$PbCrO_4$	solubility:	very slightly sol in water, sol in strong acids and alkalies

potassium chromate[16]

synonyms:	chromic acid, potassium salt; dipotassium monochromate		
CAS number:	7789-00-6	appearance:	rhombic yellow crystals
molecular weight:	194.19	melting point:	975 °C
chemical formula:	K_2CrO_4	solubility:	sol in water, insol in alcohol

potassium dichromate[17]

synonyms:	potassium bichromate

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[10] Occupational Exposure to Hexavalent Chromium- 71 FR at 10104, www.osha.gov/pls/oshaweb/owadisp.show_document?p_table=FEDERAL_REGISTER&p_id=18599 (accessed 2/28/06).

[11] *Documentation of the Threshold Limit Values and Biological Exposure Indices, Supplement to the Sixth Edition*, American Conference of Governmental Industrial Hygienists, Inc.: Cincinnati, OH, 1996, p Supplement:Chromium– 1.

[12] OSHA Chemical Sampling Information. http://www.osha.gov/dts/chemicalsampling/data/CH_228697.html (accessed 7/10/2006).

[13] OSHA Chemical Sampling Information. http://www.osha.gov/dts/chemicalsampling/toc/toc_chemsamp.html (accessed 11/15/04).

[14] O'Neil, M.J., Sr. Ed., *The Merck Index,* 13th ed, Merck & Co. Inc.: Whitehouse Station, NJ, 2001, p 387.

[15] O'Neil, M.J., Sr. Ed., *The Merck Index,* 13th ed, Merck & Co. Inc.: Whitehouse Station, NJ, 2001, p 968.

[16] O'Neil, M.J., Sr. Ed., *The Merck Index,* 13th ed, Merck & Co. Inc.: Whitehouse Station, NJ, 2001, p 1368.

[17] O'Neil, M.J., Sr. Ed., *The Merck Index,* 13th ed, Merck & Co. Inc.: Whitehouse Station, NJ, 2001, p 1368.

CAS number: 7778-50-9 appearance: orange-red crystals
molecular weight: 294.18 melting point: 398 °C
chemical formula: $K_2Cr_2O_7$ solubility: sol in water

zinc chromate[18]
synonyms: zinc chromate hydroxide
CAS number: 13530-65-9 appearance: yellow crystals
molecular weight: 183.39 melting point: 316 °C
chemical formula: $CrH_2O_4 \cdot Zn$ solubility: very slightly sol in water

This method was evaluated according to the OSHA SLTC “Evaluation Guidelines for Air Sampling Methods Utilizing Chromatographic Analysis”[19]. The Guidelines define analytical parameters, specify required laboratory tests, statistical calculations and acceptance criteria. The analyte air concentrations throughout this method are based on the recommended sampling and analytical parameters.

1.2 Limit defining parameters

1.2.1 Detection limit of the analytical procedure

The detection limit of the analytical procedure is 0.0081 ng Cr (VI). This is the amount of analyte that will give a detector response that is significantly different from the response of a reagent blank. (Section 4.1)

1.2.2 Detection limit of the overall procedure

The detection limits of the overall procedure are 0.94 ng/sample (0.98 ng/m^3) for Cr (VI) on NaOHqz, 1.00 ng/sample (1.0 ng/m^3) for Cr (VI) on PVC filters extracted with BE/PBM, and 0.80 ng/sample (0.83 ng/m^3) for Cr (VI) on PVC filters extracted with SPE/PBM. These are the amounts of Cr (VI) spiked on the respective sampler that will give detector responses that are significantly different from the responses of the respective sampler blanks. (Section 4.2)

1.2.3 Reliable quantitation limit

The reliable quantitation limits are 3.12 ng/sample (3.2 ng/m^3) for Cr (VI) on NaOHqz, 3.33 ng/sample (3.5 ng/m^3) for Cr (VI) on PVC filters extracted with BE/PBM, and 2.67ng/sample (2.9 ng/m^3) for Cr (VI) on PVC filters extracted with SPE/PBM. These are the amounts of Cr (VI) spiked on the respective samplers that will give detector responses that are considered the lower limits for precise quantitative measurements. (Section 4.2)

1.2.4 Instrument calibration

The standard error of estimate is 0.404 ng/mL over the range of 25 to 200 ng/mL. This range corresponds to 0.25 to 2 times the TWA target concentration. (Section 4.3)

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[18] Lewis, R.J. Sr., Ed., *Hazardous Chemicals Desk Reference,* Van Nostrand Reinhold, New York, 1997, p 1240.

[19] Evaluation Guidelines For Air Sampling Methods Utilizing Chromatographic Analysis, http://www.osha.gov/dts/sltc /methods/chromguide/index.html (accessed 11/15/05).

1.2.5 Precision

The precision of the overall procedure at the 95% confidence level for the ambient temperature 14-day storage test for samples on NaOHqz was ±9.92% and the precision for PVC filters was ±10.0%. These include an additional 5% for sampling pump variability. (Section 4.4)

1.2.6 Recovery

The recovery of Cr (VI) from samples used in two-week storage tests remained above 96.3% for NaOHqz and above 96.4% for PVC filters when the samples were stored at 23 °C. (Section 4.5)

1.2.7 Reproducibility

Six samples each were prepared with the two types of samplers, by spiking 960 ng of Cr (VI) onto them, and then drawing 960 liters air at 80% RH and 23 °C through them. These were submitted for analysis at SLTC. The samples were analyzed according to a draft copy of this procedure after 7 and 10 days of storage at 23 °C for NaOHqz and PVC filters, respectively. No individual sample result deviated from its theoretical value by more than the precision reported in Section 1.2.5. (Section 4.6)

2. Sampling Procedure

All safety practices that apply to the work area being sampled should be followed. The sampling equipment should be attached to the worker in such a manner that it will not interfere with work performance or safety.

2.1 Apparatus

Samples are collected using a personal sampling pump calibrated, with the sampling device attached, to within ±5% of the recommended flow rate.

Samples from chromium plating operations are collected on 37-mm NaOHqz. For this evaluation binderless quartz fiber filters were purchased from Millipore Inc. (catalog no. AQFA03700, lot R5EN76208) and coated with NaOH as described below. The filters are placed into two-piece cassettes and sampled closed face. It is not necessary to use a BUP with NaOHqz. It is important to submit a blank sample from the same lot of NaOHqz with each set of samples as there may be a background amount of Cr (VI). The amount of Cr (VI) found on binderless quartz fiber filters varied from manufacturer to manufacturer and from lot to lot, with amounts of 0 to 50 ng. The amount of Cr (VI) found in NaOH also varied by manufacturer and lots, with amounts of 0 to 20 ng.

NaOHqz are prepared by placing binderless quartz fiber filters onto the rim of clean glass beakers (20 or 50-mL size), pipetting 0.5 mL of a 1.0 N NaOH (4 g NaOH in 100 mL of DI water) solution onto each filter, and allowing the filter to dry under nitrogen at either ambient temperature for four hours or in a vacuum oven at 100 °C for 30 min. After filters are dry, analyze four to determine the amount of background Cr (VI). If the background Cr (VI) is above 0.1 µg fresh filters should be prepared after the source of the contamination is identified. The source of contamination may be NaOH, binderless quartz fiber filters, or both. Binderless quartz fiber filters can be heated in BE and then rinsed in DI water to remove the contamination. The filters can be stored in room air for 1 month or under nitrogen for 4 months. The filters used in this evaluation were prepared at SLTC.

Samples from chromium plating operations can also be collected on 37-mm 5-µm PVC filter with BUP. For this evaluation, the PVC filters and BUP were purchased from Mine Safety

Appliances Inc. (catalog no. 625413, lot 01930). The filters are placed into two-piece cassettes and sampled closed face. These samples must either be analyzed, or be stabilized immediately upon arrival at the analytical laboratory as described in Section 3.4, within 6 days of sampling.

Samples from other operations are collected on 37-mm or 25-mm 5-μm PVC filters with BUPs. For this evaluation, PVC filters and BUPs were purchased from Mine Safety Appliances Inc. (catalog no. 625413, lot 01930), and the 25-mm PVC filters were purchased from Millipore (catalog no. 502500, lot R4AS27341). The filters are placed into two-piece cassettes and sampled closed face.

Samples from other operations are collected on 37-mm 5-μm PVC filters with BUPs. For this evaluation, PVC filters and BUPs were purchased from Mine Safety Appliances Inc. (catalog no. 625413, lot 01930). The filters are placed into two-piece cassettes and sampled closed face.

2.2 Reagents

None required

2.3 Technique

Immediately before sampling, remove the top and end plugs from the cassette. All filters should be from the same lot.

Attach the cassette to the sampling pump so that it is in an approximately vertical position with the inlet facing down during sampling near the worker's breathing zone. Position the sampling pump, cassette, and tubing so it does not impede work performance or safety.

Air being sampled should not pass through any hose or tubing before entering the cassette.

After sampling for the appropriate time, remove the sampler, and replace the top and end plugs. Wrap each sample end-to-end with a Form OSHA-21 seal.

Submit at least one blank sample with each set of samples, making sure that it is from the same lot as the filters used for sampling. Handle the blank sampler in the same manner as the other samples except draw no air through it.

Record sample volume (in liters of air) for each sample, identify the type of operation, and identify any potential interference. It is important to identify the operation because it affects the sample preparation procedure that is used.

All samples should be shipped overnight to the analytical laboratory within 24 hours of sampling.

2.4 Sampler capacity (Section 4.7)

It was not possible to safely generate a Cr (VI) test atmosphere at SLTC; consequently retention efficiency studies were performed to test the ability of the sampler to retain Cr (VI). A collection efficiency of 94.5% ±3.5% has been reported for chromic acid mist collected on PVC filters by other researchers[20].

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[20] Dutkiewicz, R., Konczalik, J., Przechera, M., Assesment of the Colorimetric Methods of Determination of Chromium in Air and Urine by Means of Radioisotope Techniques. *Acta Pol. Pharm.* **1969**, *Vol.26*, 168-176.

A retention efficiency test for Cr (VI) spiked on NaOHqz was performed by spiking 1920 ng of Cr (VI) onto the filters and placing them into polystyrene cassettes. A second cassette containing a clean NaOHqz was placed behind the spiked filter and cassette. These sampling trains had 960 liters air at 80% relative humidity and 23°C drawn through them. There was no Cr (VI) found on the back-up filters. The average recovery was 98.1% for the spiked filters.

A retention efficiency test for Cr (VI) on PVC filters was performed by spiking 1920 ng of Cr (VI) onto the filters and placing them together with a BUP into polystyrene cassettes. A second cassette containing a clean PVC filter and BUP was placed behind the spiked filter and cassette. These sampling trains had 960 liters air at 80% relative humidity and 23°C drawn through them. There was no Cr (VI) found on the filters of the back-up samplers. The average recovery was 97.5% for the 37-mm PVC filters, and 97.8% for the 25-mm PVC filters.

2.5 Extraction efficiency (Section 4.8)

It is the responsibility of each analytical laboratory to independently determine extraction efficiency because their reagents and laboratory techniques may be different than those used in this evaluation and could influence results.

2.5.1 NaOHqz extracted with BE/PBM

The mean extraction efficiency for soluble Cr (VI) from NaOHqz over the range of RQL to 2 times the target concentration (3 to 1920 ng per sample) extracted with BE/PBM was 97.7%. The extraction efficiency was not affected by the presence of water (mean recovery of 97.4%).

Extracted samples remain stable for at least 24 h.

2.5.2 PVC filters extracted with BE/PBM

The mean extraction efficiency for soluble Cr (VI) from PVC filters over the range of RQL to 2 times the target concentration (3 to 1920 ng per sample) extracted with BE/PBM was 97.2%. The extraction efficiency was not affected by the presence of water (mean recovery of 97.1%).

The mean extraction efficiency for insoluble Cr (VI) from PVC filters over the range of RQL to 2 times the target concentration (3 to 1920 ng per sample) extracted with BE/PBM was 97.7%. The extraction efficiency was not affected by the presence of water (mean recovery of 98.1%).

Extracted samples for both soluble and insoluble Cr (VI) remain stable for at least 24 h.

2.5.3 PVC filters extracted with SPE/PBM

The mean extraction efficiency for soluble Cr (VI) from PVC filters over the range of RQL to 2 times the target concentration (3 to 1920 ng per sample) extracted with SPE/PBM was 98.4%. The extraction efficiency was not affected by the presence of water (mean recovery of 98.4%).

The mean extraction efficiency for insoluble Cr (VI) from PVC filters over the range of RQL to 2 times the target concentration (3 to 1920 ng per sample) extracted with SPE/PBM was 97.7%. The extraction efficiency was not affected by the presence of water (mean recovery of 98.1%).

Extracted samples for both soluble and insoluble Cr (VI) remain stable for at least 24 h.

2.6 Recommended sampling time and sampling rate

Sample for Cr (VI), in chromium plating operations, using either NaOHqz or PVC filters for 480 min at 2.0 L/min (960 L). Sample for Cr (VI), in all other operations, using PVC filters for 480 min at 2.0 L/min (960 L).

2.7 Interferences, sampling (Section 4.9)

NaOHqz

Low humidity

The ability of NaOHqz to retain Cr (VI) in a relatively dry atmosphere was tested by spiking 1920 ng of Cr (VI) onto each of three filters and placing them into polystyrene cassettes. The cassettes then had 960 liters of air at 19% RH and 24 °C drawn through them at a flow rate of 2 L/min. All of the samples were immediately analyzed. The mean recovery was 97.3% of theoretical.

Low concentration

The ability of NaOHqz to retain Cr (VI) at low concentration was tested by spiking 96 ng of Cr (VI) onto each of three filters and placing them into polystyrene cassettes. The cassettes then had 960 liters of air at 79% RH and 23 °C drawn through them at a flow rate of 2 L/min. All of the samples were immediately analyzed. The mean recovery was 97.2% of theoretical.

Interference

The main sampling interference in chromium plating is the acid in the plating bath (mainly sulfuric acid but occasionally phosphoric acid or other mineral acids) and Cr (III). The ability of NaOHqz to retain Cr (VI) was tested by spiking 960 ng of Cr (VI) onto each of three filters, together with 100 ng of Cr (III) and 50 ng of H_2SO_4, and placing the filters into polystyrene cassettes. The cassettes then had 960 liters of air at 79% RH and 23 °C drawn through them at a flow rate of 2 L/min All of the samples were immediately analyzed. The mean recovery was 99.4% of theoretical. Tests were also performed to determine if the acid affected storage stability. Samples were prepared by spiking NaOHqz with 960 ng of soluble Cr (VI) and 50 ng of H_2SO_4 and the filters were allowed to dry. The spiked NaOHqz had 960 L of air at 80% RH and 23 °C drawn through them. On day 14 the recovery was 96.0% for samples stored at ambient temperature (about 22 °C) and 95.5% for samples stored at refrigerated temperature (4 °C). These tests showed that any interference from the acid was minimal (Section 4.9.1).

PVC filter

Low humidity

The ability of PVC filters to retain Cr (VI) in a relatively dry atmosphere was tested by spiking 1920 ng of Cr (VI) onto each of three filters, and placing them into polystyrene cassettes. The cassettes then had 960 liters of air at 20% RH and 23 °C drawn through them at a flow rate of 2 L/min. All of the samples were immediately analyzed. The mean recovery was 98.4% of theoretical.

Low concentration

The ability of PVC filters to retain Cr (VI) at low concentration was tested by spiking 96 ng of Cr (VI) onto each of three filters, and placing them into polystyrene cassettes. The cassettes then had 960 liters of air at 79% RH and 23 °C drawn through them at a flow rate of 2 L/min. All of the samples were immediately analyzed. The mean recovery was 96.5% of theoretical.

Interference (Section 4.9.2)

Reducing metal species have the potential to reduce Cr (VI) to Cr (III). Also, Cr (III) may oxidize to Cr (VI) when heated in an alkaline solution. These interferences are greatly reduced by the addition of PBM to the BE, causing the other metal species to precipitate. The recovery of Cr (VI) (1000 ng) in a 1:10 ratio with Fe (II) was 29.2% with BE alone, and 92.7% with BE/PBM. The recovery of Cr (VI) (1000 ng) in a 1:10 ratio with Cr (III) was 103% with BE alone, 99.3% with BE/PBM, 104.7% with SPE alone and 100.6% with SPE/PBM. These tests showed that PBM was effective in avoiding this interference.

The main interference in welding operations is Fe (II) because it reacts with Cr (VI) to form Cr (III). While the addition of PBM keeps the Fe (II) from reacting in extracted samples, Fe (II) may react with Cr (VI) on the PVC filter when it is stored before analysis. A storage test was performed by spiking PVC filters with 960 ng of soluble Cr (VI) and 0.5 mg Fe (II) separately on differing spots on the same filter, and allowing the filters to dry. The dried spikes on the same filter were rubbed together to mix them. Cr (VI) and Fe (II) react slowly in the dry state but they react more quickly in a water solution to form Cr (III). For this reason, Cr (VI) and Fe (II) could not be placed in the same solution, or the solutions spiked on top of each other, but instead had to be mixed together in the dry state. The spiked PVC filters then had 960 L of air at 80% RH and 23 °C drawn through them. The Evaluation Guidelines for Air Sampling Methods Utilizing Chromatographic Analysis state that “A change in recovery of more than 10% in 15 days is a significant uncorrectable bias and must be avoided”.[21] The loss in recovery exceeded 10% after 7 days, showing that welding samples must be analyzed within 8 days of collection.

The presence of acid in chrome plating workplaces causes a negative interference due to reaction between Cr (VI) and acid to form Cr (III). Most chrome plating baths contain H_2SO_4, so a mixture of H_2SO_4 and Cr (VI) was prepared in water to spike the filters. Storage stability tests were performed in which PVC filters were spiked with 960 ng of soluble Cr (VI) and 50 ng of H_2SO_4 and allowed to dry. The spiked PVC filters then had 960 L of air at 80% RH and 23 °C drawn through them before storage. The loss in recovery exceeded 10% after 6 days, requiring that the samples be analyzed within 6 days of collection. The results showed a recovery of 74.5% on day 14 for samples stored at ambient temperature, and 73.8% for refrigerated samples. To circumvent this negative bias, another test was performed with similarly spiked filters, but these filters were placed into 5 mL of BE immediately after drawing humid air through them. The recoveries on day 14 were 94.2% for ambient and 96.0% for refrigerated samples. This experiment shows that chromium plating samples can be stabilized as described.

The hardened matrix of paint samples encapsulates Cr (VI) and prevents it from being extracted. Two separate extractions are necessary to break down the paint matrix and liberate Cr (VI). The recoveries were 46.2% for BE/PBM, 69.8% for SPE/PBM, and 101% for BE/PBM followed by SPE/PBM, showing that a two step extraction is necessary.

3. Analytical Procedure

Adhere to the rules set down in your Chemical Hygiene Plan as required by the Code of Federal Regulations[22]. Avoid skin contact and inhalation of all chemicals and review all MSDSs before beginning this analytical procedure.

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[21] Evaluation Guidelines For Air Sampling Methods Utilizing Chromatographic Analysis, http://www.osha.gov/dts/sltc /methods/chromguide/index.html (accessed 11/15/03).

[22] Occupational Exposure to Hazardous Chemicals in Laboratories, http://www.osha.gov/pls/oshaweb/ owadisp.show_document?p_ table=STANDARDS&p_id=10106 (accessed 2/28/06)

3.1 Apparatus

Ion chromatograph with a UV-vis detector and a post-column reagent delivery system. A Dionex DX-500 ion chromatograph with a GP50 gradient pump, an AD25 absorbance detector, an AS50 autosampler, a PC-10 pneumatic controlled post-column reagent delivery system, and a reaction coil were used in this evaluation.
IC column and guard column that can separate Cr (VI) from potential interferences. A Dionex IonPac AS7 analytical column (250-mm × 4-mm i.d.) and a Dionex IonPac NG1 guard column (50-mm × 4-mm i.d.) were used in this evaluation.

A means to integrate chromatograms. Dionex Peaknet software, and Waters Millennium[32] data systems were used in this evaluation.

All glassware including centrifuge tubes used in this analysis should first be cleaned in a laboratory dishwasher, then further cleaned by soaking in 10% nitric acid solution for 1 hour, and then rinsed three times with DI water. Under no circumstance should chromic acid cleaning be used. It is best if glassware used for the analysis of Cr (VI) be reserved for this purpose only so that maximum analytical sensitivity and absence of outside contamination can be maintained.

Class A volumetric flasks, 10-mL and other convenient sizes for preparing standards.

Class A volumetric pipets and calibrated micropipets, for making analytical standards.

Erlenmeyer flasks, 50-mL or larger, for sample extraction.

Micro-analytical balance capable of weighing to at least 0.01 mg. A Ohaus Galaxy 160D balance was used in this evaluation.

Polyethylene bottles, 1-L size or larger, for storing extraction solutions.

Hotplate with temperature adjustable to between 95 and 135 °C and placed in a fume hood. A Lindberg/Blue model 53015 hotplate was used in this evaluation.

Optional: Centrifuge for spinning down precipitate in samples. An International Equipment Company Centra CL3 centrifuge was used in this method.

3.2 Reagents

DI water, 18 MΩ-cm. A Barnstead NanoPure Diamond system was used to purify the water for this evaluation.

Sodium carbonate [CAS no. 497-19-8], reagent grade. Mallinckrodt 99+% lot 7527 KHKC was used in this evaluation.

Sodium bicarbonate [CAS no. 144-55-8], reagent grade. Baker Analyzed reagent 99.9% lot D12721 was used in this evaluation.

Sodium hydroxide [CAS no. 1310-73-2], reagent grade. Aldrich 99.998% lot 11416BC was used in this evaluation.

Potassium dichromate [CAS no. 7778-50-9], reagent grade. JT Baker reagent grade 99% lot 715426 and Acros reagent grade 99%+ lot A010583303 were used in this evaluation.

Magnesium sulfate [CAS no. 7487-88-9], anhydrous, reagent grade. ChemPure reagent grade 99% lot M172KDHM was used in this evaluation.

Ammonium sulfate [CAS no. 7783-20-2], reagent grade. Aldrich 99+% lot OO427TQ was used in this evaluation.

Ammonium hydroxide [CAS no. 1336-21-6], 29% solution. Baker analyzed reagent 28.9% NH_4OH lot 611248 was used in this evaluation.

1,5-Diphenylcarbazide (DPC) [CAS no. 140-22-7], reagent grade. Aldrich 99+% lot 03017AR was used in this evaluation.

Methyl alcohol [CAS no. 67-56-1], HPLC grade. Fisher Optima 99.9% lot 966306 was used in this evaluation.

Sulfuric acid [CAS no. 7664-93-9], concentrated. JT Baker Instra-analyzed 96.8% lot E24049 was used in this evaluation.

Nitric acid [CAS no. 7697-37-2], concentrated (69-70%). JT Baker Instra-analyzed 69.0-70.0% lot N46048 was used in this evaluation.

Potassium hydrogen phosphate trihydrate [CAS no. 16788-57-1], reagent grade. Aldrich 99+% lot 01525MN was used in this evaluation.

Potassium dihydrogen phosphate [CAS no. 7778-77-0], reagent grade. Aldrich 99+% lot 06327KQ was used in this evaluation.

Nitric acid solution (10%): Place about 500 mL of DI water in a 1-L volumetric flask, add 100 mL of concentrated nitric acid, then dilute up to the mark with DI water.

Buffer/extraction (BE) solution (2% $NaHCO_3$ with 10% Na_2CO_3): Place about 500 mL of DI water in a 1-L volumetric flask, add 20 g of $NaHCO_3$, swirl to dissolve, then add 100 g of Na_2CO_3, and dilute up to the mark with DI water. Shake to dissolve or use an ultrasonic bath. Store the solution in a polyethylene bottle.

Spray-paint extraction (SPE) solution (5% NaOH + 7.5% Na_2CO_3): Dissolve 50 g of NaOH and 75 g of Na_2CO_3 in about 500 mL of DI H_2O contained in a 1.0-L volumetric flask. Allow the solution to cool to room temperature, and then dilute to the mark with DI H_2O. Transfer and store this solution in a tightly capped polyethylene bottle. Use this solution only for the second extraction of samples from spray-paint operations. Prepare this solution monthly.

Magnesium sulfate solution: Place about 50 mL of DI water in a 100-mL volumetric flask, add 9.9 g of anhydrous magnesium sulfate, mix well, and dilute up to the mark with DI water.

Phosphate buffer solution (0.5 M KH_2PO_4 with 0.5 M $K_2HPO_4 \cdot 3H_2O$): Place about 500 mL of DI water in a 1-L volumetric flask, add 68 g of KH_2PO_4 and 114 g of $K_2HPO_4 \cdot 3H_2O$, swirl to dissolve and dilute up to the mark with DI water.

Phosphate buffer/$MgSO_4$ solution (PBM): Place 50 mL of phosphate buffer in a 100-mL beaker, then add 25 mL of magnesium sulfate solution, and mix well. Prepare this solution fresh before each analysis, because it is stable for only 4 hours.

Dilute Buffer Extraction/Phosphate buffer/$MgSO_4$ solution (DBE/PBM): Pipette 50 mL of BE solution into a 100-mL volumetric flask, add 15 mL of PBM solution, dilute up to the mark with DI water, and mix. Magnesium hydroxide will form and slowly precipitate from solution. Allow the precipitate to settle for at least 60 minutes, or centrifuge at 3,200 rpm for 5-10 min. Transfer the “clear” solution to a beaker for use in preparation of working standards. Try to avoid transferring any precipitate as it will clog the IC.

Eluent [250 mM $(NH_4)_2SO_4$ with 100 mM NH_4OH]: Place about 500 mL of DI water in a 1-L volumetric flask, add 6.5 mL of 29% ammonium hydroxide, then add 33 g of ammonium sulfate and mix well. Dilute to the mark with DI water. Degas the eluent before use. The eluent was degassed with house vacuum and an ultrasonic bath in this evaluation. Transfer the solution to the eluent container of the IC.

Post-column derivatization reagent (2.0 mM DPC in 90:10 1 N H_2SO_4:methyl alcohol): Place 0.5 g of DPC in a 100-mL volumetric flask, dilute to the mark with methyl alcohol, and mix well. In a 1-L volumetric flask place about 500 mL of DI water, add 28 mL of concentrated sulfuric acid, mix well, and allow the solution to cool. When the sulfuric acid solution has cooled to room temperature, add the DPC/methanol solution, dilute up to the mark with DI water, mix well, and again allow the solution to cool before placing it in the post-column reservoir. This solution is stable for 3 days. This solution must be freshly prepared and be at room temperature to obtain maximum sensitivity.

3.3 Standard preparation

Prepare stock standards containing about 100 µg/mL of Cr (VI) by dissolving approximately 0.2828 g of $K_2Cr_2O_7$ in 1.000 L of DI water. (For example: the calculation for a stock standard is: (0.2828 g $K_2Cr_2O_7$/liter) × (1000 mg/g) × (1000 µg/mg) × (L/1000 mL) × (MW Cr/MW $K_2Cr_2O_7$ = 51.996/294.18) × (2 moles of Cr in $K_2Cr_2O_7$) = 100 µg/mL Cr (VI).) Prepare this solution every 3 months. Make all dilutions of the stock standard with DBE/PBM solution in order to matrix match standards with samples. The working range for analytical standards is 0.3 to 200 ng/mL. Prepare these diluted analytical standards weekly.

Bracket sample concentrations with analytical standard solutions. If sample concentrations fall outside the range of prepared standards, prepare and analyze additional standards to confirm instrument response, or dilute high samples with DBE/PBM solution and reanalyze the diluted samples.

3.4 Sample preparation

Primary extraction for all filters

PVC and NaOHqz filters (except PVC filters used to sample chromium plating operations and that have been stabilized as described below) are extracted using the primary extraction procedure that consists of several steps that must be performed in the given order. These steps cause formation of a precipitate that traps metal interferences and prevents them from reacting with Cr (VI).

Adjust the hotplate temperature to between 100-130 ºC which is below the boiling point of BE solution. A hot water bath set at 100 ºC may be used.

Each sample is prepared as follows: remove the filter from the cassette and place it in a labeled 50-mL Erlenmeyer flask. Wipe the inside walls of the cassette with the rough side of a PVC filter wetted with a drop of DBE/PBM and place it into a separate labeled 50-mL Erlenmeyer flask. The interior walls of the blank-sample cassettes should also be wiped.

Add 1.5 mL of PBM solution to each Erlenmeyer flask and swirl to wet the filter. Next add 5 mL of BE solution and mix the solution well before proceeding to the next sample. It is important to add the PBM solution first because the freshly precipitated magnesium hydroxide that forms upon the addition of the BE solution suppresses interference from other metal ions. This precipitation occurs immediately upon mixing, so it is important that both sides of the filter are wetted.

Samples from chromium plating operations collected on PVC filters must either be analyzed within 6 days of sampling or be stabilized immediately upon arrival at the analytical laboratory. Samples are stabilized by removing the filters from the cassettes and placing them in labeled 20-mL glass vials containing 5 mL of BE. The interior walls of the sampling cassette should be wiped with the rough side of a PVC filter that has been wetted with a drop of DBE/PBM, and then also stabilized by placing it into a separate labeled vial containing 5 mL of BE (Section 4.8.6). Acids from chromium plating operations are neutralized by the BE solution, and this allows samples to be stored for up to two weeks before analysis. Just prior to heating the samples for the hot extraction, add 1.5 mL of PBM. Heat the vials (without caps) on a hotplate or in a hot water bath. The order of BE and PBM solution addition is reversed here as the main interference at room temperature is acids. Cr (III) does not convert to Cr (VI) at room temperature. The addition of PBM prior to heating precipitates out the Cr (III), preventing it from forming Cr (VI) during heating.

Heat chromium plating and welding samples at 100-130 ºC for 30 min. Heat paint samples at the same temperature for 90 min. Carefully watch the process to prevent the samples from boiling or evaporating to dryness. If the samples do boil or evaporate to dryness the Cr (VI) will change to Cr (III), causing low results. If the solution begins to boil, squirt in 1-2 mL of DI water to cool the solution, remove the flask from the hotplate to cool for about 5 min, and then return it to hotplate to heat for the remaining amount of time.

Allow the samples to cool to room temperature. Quantitatively transfer each solution to a 10-mL volumetric flask using DI water, and dilute up to the mark with DI water. Allow the samples to sit for 4 hours for the precipitate to settle, or centrifuge them at 3200 rpm for 5 to 10 minutes. Carefully transfer the supernatant to an autosampler vial. Make sure that none of the precipitate is transferred because it will clog the autosampler and/or the IC.

Secondary extraction for spray paint samples

Extract filter samples and cassette wipes from spray painting operations a second time to further break apart the paint matrix, thereby freeing the Cr (VI) for analysis. After the primary extraction is completed and the BE/PBM solution has been removed, extract the PVC filter in the Erlenmeyer flask again by adding 1.5 mL of PBM solution and then 5 mL of SPE solution. Swirl the flask slowly until the white precipitate occurs.

Heat the solution at approximately 100-130 ºC with occasional swirling for 90 min. Allow extra extraction time for heavily loaded samples. Do not allow the solution to boil. If the solution does begin to boil squirt in 1-2 mL of DI water to cool it, remove the flask from the hotplate to cool for about 5 min, and then return the flask to hotplate for the remaining amount of time.

Allow the secondary extraction solution to cool to room temperature. Quantitatively transfer each solution to a 25-mL volumetric flask using DI water, and dilute up to the mark with DI water and shake. Due to the high concentration of NaOH in SPE, the samples are diluted to 25 mL to obtain a closer match in concentration between samples and standards. Diluting to 10 mL may cause the ion chromatograph to develop a clog. Either transfer the contents to a centrifuge tube and spin down the precipitate for 5 min at 3200 rpm, or allow the solution to settle for 4 hours. Transfer the clear supernatant to the autosampler vials for analysis. Be careful to not transfer any of the precipitate because it will clog the autosampler and/or the IC.

3.5 Analysis

It may be necessary to pacify the column with a standard containing about 10 ng/mL of Cr (VI) to detect levels less than 1 ng/mL.

IC conditions:

columns: IonPac AS7 analytical column (250-mm × 4-mm i.d.) and IonPac NG1 guard column (50-mm × 4-mm i.d.) at ambient temperature
flow rate: 0.9 mL/min
eluent: 250 mM $(NH_4)_2SO_4$ with 100 mM NH_4OH
pump pressure: ~1200 psi
post-column derivatization solution: ~0.6 mL/min of 2.0 mM DPC in 90:10 1 N H_2SO_4:methyl alcohol
UV detector: 540 nm
injection size: 100 µL
retention time: 5.3 min
output range: 0.1 absorbance unit full scale (AUFS)

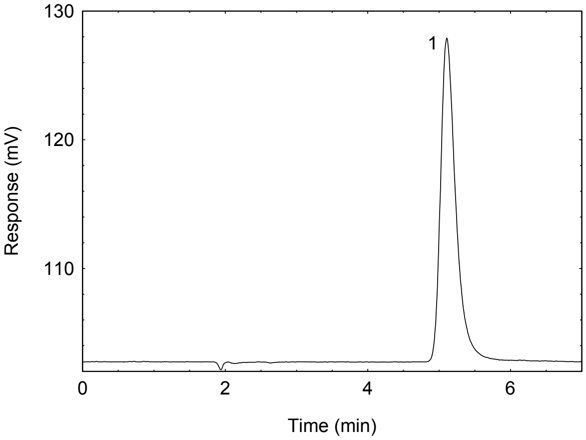

Figure 3.5.1. A chromatogram of 100 ng/mL Cr (VI). [Key: 1) Cr (VI).]

An external standard (ESTD) calibration procedure is used to prepare a calibration curve from the analysis of analytical standards. The calibration curve is prepared daily (Figure 3.5.2.). Bracket samples with analytical standards.

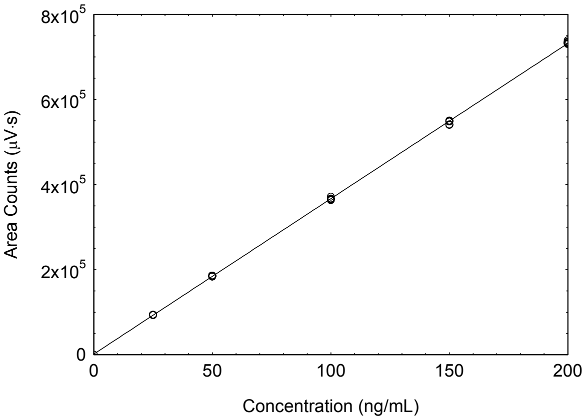

Figure 3.5.2. Calibration curve of Cr (VI). (y = 3650x + 1901)

3.6 Interferences (analytical)

Any compound that produces a detector response at 540 nm and has a similar retention time as Cr (VI) is a potential interference. If potential interferences were reported, they should be considered before samples are extracted. Generally, chromatographic conditions can be altered to separate any interference from the analyte.

When necessary, the identity of an analyte peak may be confirmed with additional analytical data, such as analysis with another analytical column (Section 4.10). The presence of a co-eluting species that does not react with DPC can be tested by injecting the sample with no post-column derivatizing reagent being added.

3.7 Calculations

Perform a correction for each NaOHqz or PVC filter extraction result with a blank from the same lot of medium.

The result for the BE/PBM extraction is:

$$A_{BE/PBM} = [Cr\ (VI)_{BE/PBM}\ x\ (Sol\ Vol)_{BE/PBM}] - [Cr\ (VI)_{BE/PBMblank}\ x\ (Sol\ Vol)_{BE/PBMblank}]$$

where:

$A_{BE/PBM}$ = amount found on filter (ng) from BE/PBM extraction
$Cr\ (VI)_{BE/PBM}$ = total ng/mL Cr (VI) on filter from BE/PBM extraction
$(Sol\ Vol)_{BE/PBM}$ = sample solution volume (usually 10 mL, but if dilution was necessary make appropriate calculations here)
$Cr\ (VI)_{BE/PBMblank}$ = total ng/mL Cr (VI) on blank from BE/PBM extraction
$(Sol\ Vol)_{BE/PBMblank}$ = blank solution volume (10 mL)

The result for the SPE secondary extraction (spray paint operations only) is:

$$A_{SPE/PBM} = [Cr\ (VI)_{SPE/PBM}\ x\ (Sol\ Vol)_{SPE/PBM}] - [Cr\ (VI)_{SPE/PBMblank}\ x\ (Sol\ Vol)_{SPE/PBMblank}]$$

where:

$A_{SPE/PBM}$ = amount found on filter (ng) from SPE/PBM extraction
$Cr\ (VI)_{SPE/PBM}$ = total ng/mL Cr (VI) on filter from SPE/PBM extraction
$(Sol\ Vol)_{SPE/PBM}$ = sample solution volume (usually 25 mL, but if dilution was necessary make appropriate calculations here)
$Cr\ (VI)_{SPE/PBMblank}$ = total ng/mL Cr (VI) on blank from SPE/PBM extraction
$(Sol\ Vol)_{SPE/PBMblank}$ = blank solution volume (25 mL)

The result for the cassette wipe is:

$$A_{CBE} = [Cr\ (VI)_{CBE/PBM}\ x\ (Sol\ Vol)_{BE/PBM}] - [Cr\ (VI)_{CblkBE/PBM}\ x\ 10\ mL]$$

where:

A_{CBE} = amount found on cassette wipe (ng)
$Cr\ (VI)_{CBE/PBM}$ = total ng/mL Cr (VI) on cassette wipe from extraction with BE/PBM
$(Sol\ Vol)_{BE/PBM}$ = sample solution volume of cassette wipe BE/PBM extraction (usually 10 mL, but if dilution was necessary make appropriate calculations here)
$Cr\ (VI)_{CBE/PBMblk}$ = total ng/mL Cr (VI) on cassette wipe blank from extraction with BE/PBM
$10\ mL$ = cassette wipe blank solution volume of BE/PBM extraction

$$A_{CSPE} = [Cr\ (VI)_{CSPE/PBM}\ x\ (Sol\ Vol)_{SPE/PBM}] - [Cr\ (VI)_{CblkSPE/PBM}\ x\ 25\ mL]$$

$Cr\ (VI)_{CSPE/PBM}$ = total ng/mL Cr (VI) on cassette wipe from extraction with SPE/PBM
$(Sol\ Vol)_{CSPE/PBM}$ = sample solution volume of cassette wipe SPE/PBM extraction (usually 25 mL, but if dilution was necessary make appropriate calculations here)
$Cr\ (VI)_{CSPE/PBMblk}$ = total ng/mL Cr (VI) on cassette wipe blank from extraction with SPE/PBM
$25\ mL$ = cassette wipe blank solution volume of SPE/PBM extraction

The total amount of hexavalent chromium for the sample is:

$$A = \frac{A_{BE/PBM}}{E_{EBE/PBM}} + \frac{A_{SPE/PBM}}{E_{ESPE/PBM}} + \frac{A_{CBE/PBM}}{E_{EBE/PBM}} + \frac{A_{CSPE/PBM}}{E_{ESPE/PBM}}$$

where:

A = total ng Cr (VI) in sample after blank correction
$A_{BE/PBM}$ = amount found from filter (ng) BE/PBM extraction
$A_{SPE/PBM}$ = amount found from filter (ng) SPE/PBM extraction
$A_{CBE/PBM}$ = amount found on cassette wipe (ng) BE/PBM extraction
$A_{CSPE/PBM}$ = amount found on cassette wipe (ng) SPE/PBM extraction
$E_{EBE/PBM}$ = extraction efficiency for BE/PBM extraction
$E_{ESPE/PBM}$ = extraction efficiency for SPE/PBM extraction

Cr (VI) air concentration is:

$$Cr\,(VI),\ \frac{\mu g}{m^3} = \frac{A}{V}$$

where:

A = total ng Cr (VI) in sample after blank correction (ng)
V = air volume (L)

4. Backup data

General background information about the determination of detection limits and precision of the overall procedure is found in the "Evaluation Guidelines for Air Sampling Methods Utilizing Chromatographic Analysis"[23]. The Guidelines define analytical parameters, specify required laboratory tests, statistical calculations and acceptance criteria.

4.1 Detection limit of the analytical procedure (DLAP)

DLAP is measured as the mass of analyte introduced onto the chromatographic column. Ten analytical standards were prepared with equally descending increments with the highest standard containing 1 ng/mL. This is the concentration that would produce a peak approximately 10 times the response of a reagent blank near the elution time of the analyte. These standards, and the reagent blank were analyzed with the recommended analytical parameters (Millenium[32] data system used), and the data obtained were used to determine the required parameters (standard error of estimate and slope) for the calculation of the DLAP. Values of 14200 and 38.3 were obtained for the slope and standard error of estimate respectively. DLAP was calculated to be 0.0081 ng.

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[23] Evaluation Guidelines For Air Sampling Methods Utilizing Chromatographic Analysis, http://www.osha.gov/dts/sltc /methods/chromguide/index.html (accessed 11/15/03).

Table 4.1
Detection Limit of the Analytical Procedure

concentration (ng/mL)	mass on column (ng)	area counts (µV•s)
0	0	0
0.1	0.01	249
0.2	0.02	414
0.3	0.03	561
0.4	0.04	670
0.5	0.05	812
0.6	0.06	924
0.7	0.07	1066
0.8	0.08	1255
0.9	0.09	1362
1.0	0.10	1478

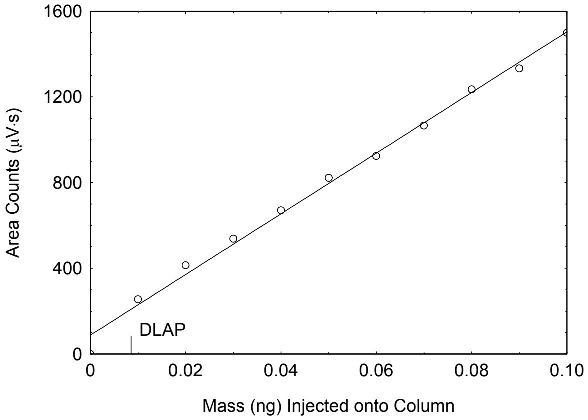

Figure 4.1. Plot of data to determine the DLAP. (y = 1.42E4x + 87.8)

4.2 Detection limit of the overall procedure (DLOP) and reliable quantitation limit (RQL)

DLOP is measured as mass per sample and expressed as equivalent air concentration, based on the recommended sampling parameters. Ten samplers were spiked with equally descending increments of analyte, such that the highest sampler loading was 10 ng/sample. This is the amount spiked on a sampler that would produce a peak approximately 10 times the response of a sample blank. These spiked samplers, and the sample blank were analyzed with the recommended analytical parameters, and the data obtained were used to calculate the required parameters (standard error of estimate and the slope) for the calculation of the DLOP. Values of 138 and 43.1 were obtained for the slope and standard error of estimate respectively for NaOHqz. DLOP was calculated to be 0.94 ng/sample (0.94 ng/m^3). Values of 131 and 43.5 were obtained for the slope and standard error of estimate respectively for PVC filters extracted with BE/PBM. DLOP was calculated to be 1.0 ng/sample (1.0 ng/m^3). Values of 136 and 36.4 were obtained for the slope and standard error of estimate respectively for PVC filters extracted with SPE/PBM. DLOP was calculated to be 1.0 ng/sample (1.0 ng/m^3).

Table 4.2.1
Detection Limit of the Overall Procedure for NaOHqz Extracted with BE/PBM

mass per sample (ng)	area counts (µV·s)
0	0
1	245
2	408
3	534
4	667
5	786
6	897
7	1011
8	1234
9	1324
10	1439

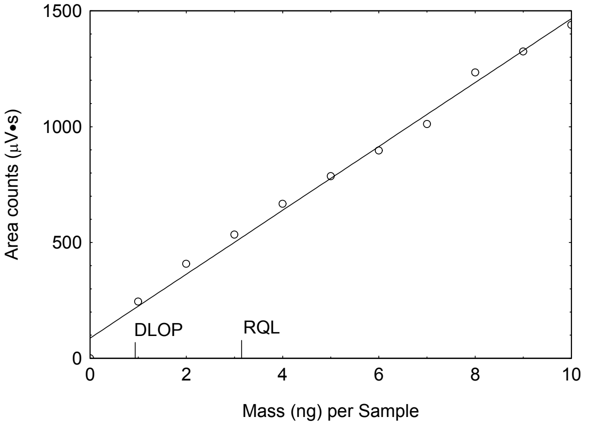

Figure 4.2.1. Plot of data in Table 4.2.1 used to determine the DLOP/RQL for NaOHqz extracted with BE/PBM. (y = 138x + 87.1)

Table 4.2.2
Detection Limit of the Overall Procedure for PVC Filters Extracted with BE/PBM

mass per sample (ng)	area counts (μV·s)
0	0
1	237
2	389
3	504
4	657
5	751
6	865
7	971
8	1170
9	1243
10	1395

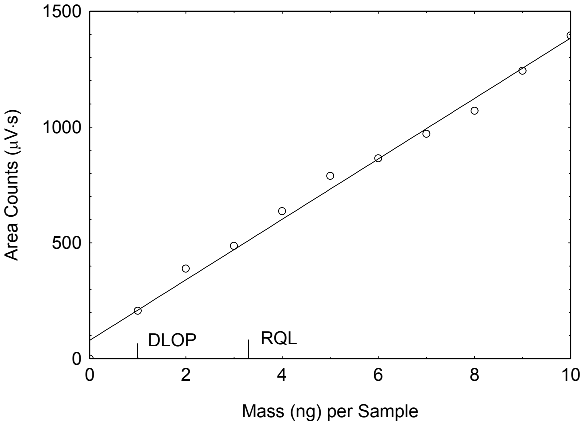

Figure 4.2.2. Plot of data in Table 4.2.2 used to determine the DLOP/RQL for PVC filters extracted with BE/PBM. (y = 131x + 79.5)

Table 4.2.3
Detection Limit of the Overall Procedure for PVC Filters Extracted with SPE/PBM

mass per sample (ng)	area counts (μV·s)
0	0
1	211
2	379
3	459
4	601
5	783
6	899
7	980
8	1188
9	1256
10	1410

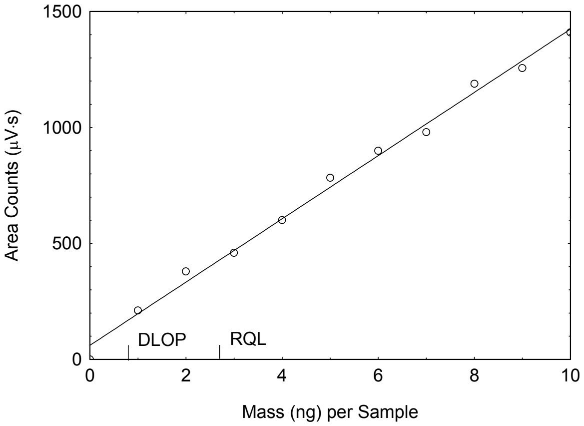

Figure 4.2.3. Plot of data in Table 4.2.3 used to determine the DLOP/RQL for PVC filters extracted with SPE/PBM. (y = 136x + 60.7)

The reliable quantitation limit (RQL) is considered the lower limit for precise quantitative measurements. It is determined from the regression line parameters obtained for the calculation of DLOP, providing 75% to 125% of the analyte is recovered. The RQL for NaOHqz is 3.12 ng per sample (3.2 ng/m^3). Recovery at this concentration is 97.8%. The RQL for PVC filters extracted with BE/PBM is 3.32 ng per sample (3.5 ng/m^3), and 2.67 ng per sample (2.9 ng/m^3) for PVC filters extracted with SPE/PBM. Recoveries at this concentration are 96.8% for BE/PBM extraction and 98.3% for SPE/PBM extraction.

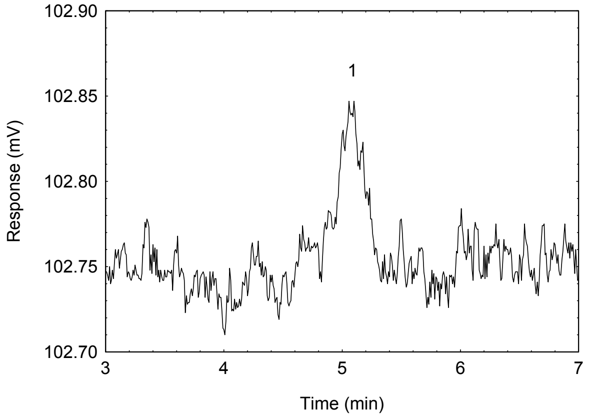

Figure 4.2.4 A chromatogram of a standard near the RQL. Key: 1 = Cr (VI).

4.3 Instrument calibration

The standard error of estimate for instrument calibration was determined from the linear regression of data points obtained from the analysis of standards over the range of 0.25 to 2 times the TWA target concentration. A calibration curve was constructed from data obtained from six injections each of five standards and it is shown in Section 3.5.2. The standard error of estimate was 0.404 ng/mL.

Table 4.3
Instrument Calibration

standard concn (ng/mL)	area counts (µV·s)					
25	94030	93397	93689	94201	92979	93434
50	185284	183909	185421	186213	183569	186102
100	366514	363184	365910	367129	371293	364923
150	549558	550123	548298	541279	539978	548234
200	732744	729885	735248	735248	735523	739088

4.4 Precision (overall procedure)

The precision at the 95% confidence level was obtained by multiplying the standard error of estimate for the appropriate storage stability test by 1.96 (the z-statistic from the standard normal distribution at the 95% confidence level). In Section 4.5, 95% confidence intervals are drawn about their respective regression lines in the storage graph figures. The precision of the overall procedure of ±9.92 % was obtained from the standard error of estimate of 5.06% in Figure 4.5.1.1 for NaOHqz. The precision of the overall procedure of ±10.0 % was obtained from the standard error of estimate of 5.10% in Figure 4.5.2.1 for PVC filters. Each precision includes an additional ±5% for sampling error.

4.5 Storage tests

Soluble Cr (VI) is defined as Cr (VI) from $K_2Cr_2O_7$ dissolved in DI water; and insoluble Cr (VI) as Cr (VI) from $PbCrO_4$ dissolved in BE solution. Lead chromate ($PbCrO_4$) is not soluble in DI water, but readily soluble in warm BE.

4.5.1 Soluble Cr (VI) spiked on NaOHqz

Storage samples were prepared by spiking NaOHqz with 960 ng of soluble Cr (VI). The spiked NaOHqz had 960 L of air at 80% RH and 23 °C drawn through them at 2 L/min. Twenty-seven storage samples were prepared. Three samples were analyzed on the day of preparation. Twelve of the filters were stored at reduced temperature (4 °C) and the other twelve were stored in a closed drawer at ambient temperature (about 22 °C). At 3 to 4-day intervals, three samples were selected from each of the two storage sets and analyzed. Sample results were not corrected for extraction efficiency. On Day 14 the recovery was 96.3% for samples stored at ambient temperature and 96.0% for samples stored at refrigerated temperature. The recovery was obtained from the equation of the storage graphs.

Table 4.5.1
Storage Test for Soluble Cr (VI) Spiked on NaOHqz

time (days)	ambient storage recovery (%)			refrigerated storage recovery (%)		
0	99.0	98.6	97.1			
3	97.4	98.8	98.3	99.0	97.4	96.6
7	96.9	98.1	98.2	98.2	96.1	96.9
10	98.0	96.9	97.2	98.1	94.9	95.9
14	94.9	95.8	96.6	97.1	95.2	96.1

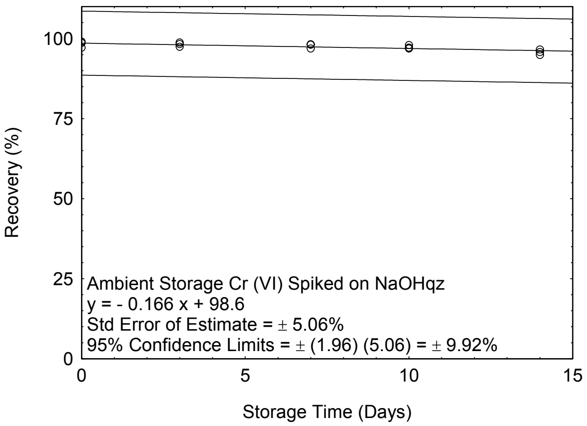

Figure 4.5.1.1. Ambient storage test for soluble Cr (VI) spiked on NaOHqz.

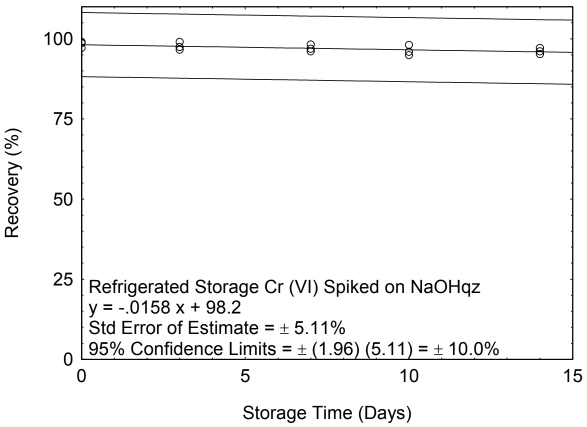

Figure 4.5.1.2. Refrigerated storage test for soluble Cr (VI) spiked on NaOHqz.

4.5.2 Soluble Cr (VI) spiked on PVC filter

Twenty-one PVC filters were spiked with 960 ng of soluble Cr (VI) and allowed to dry. The spiked filters had 960 L of air at 80% RH and 23 °C drawn through them at 2 L/min. Three samples were analyzed on the day of preparation. Nine of the filters were stored at reduced temperature (4 °C) and the other nine were stored in a closed drawer at ambient temperature (about 22 °C). At 5-day intervals, three samples were selected from each of the two storage sets and analyzed. Sample results were not corrected for extraction efficiency. The results show a recovery of 96.4% on day 15 for samples stored at ambient temperature, and 96.4% for refrigerated samples.

Table 4.5.2
Storage Test for Soluble Cr (VI) Spiked on PVC Filters

time (days)	ambient storage recovery (%)			refrigerated storage recovery (%)		
0	98.0	96.7	97.2			
5	96.9	95.9	96.0	96.7	97.4	95.6
10	95.8	96.9	96.7	97.1	98.8	95.1
15	97.8	97.6	94.5	95.2	96.4	97.3

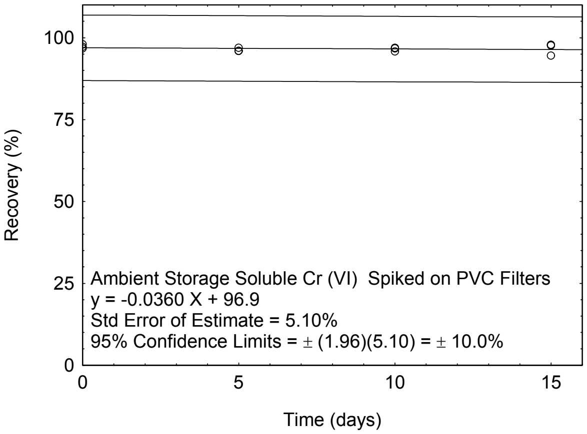

Figure 4.5.2.1. Ambient storage test for soluble Cr (VI) spiked on PVC filters.

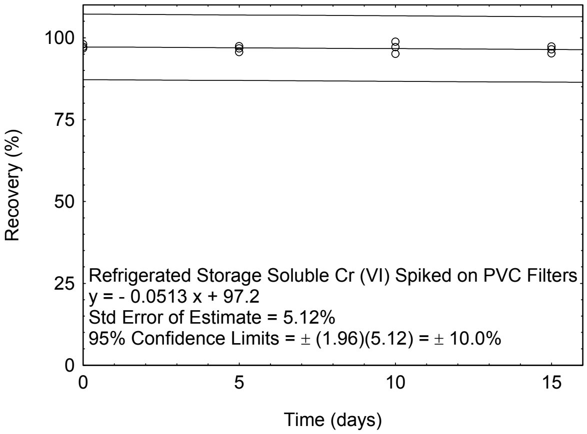

Figure 4.5.2.2. Refrigerated storage test for soluble Cr (VI) spiked on PVC filters.

4.5.3 Insoluble Cr (VI) spiked on PVC filter

This data is taken from the original version of ID-215 and it shows that insoluble Cr (VI) is stable on PVC filters for at least 30 days. Twenty-four PVC filters were spiked with 200 ng of Cr (VI) in BE and allowed to dry. The spiked filters had 960 L of air at 80% RH and 23 °C drawn through them at 2 L/min. Six samples were analyzed on the day of preparation. The other filters were stored in a closed drawer at ambient temperature (about 22°C). At 5, 15, and 30 day intervals six samples were selected and analyzed. Sample results were not corrected for extraction efficiency. The results show a recovery of 94.8% on day 30 for samples stored at ambient temperature.

Table 4.5.3
Storage Test for Insoluble Cr (VI) on PVC Filters

time (days)	ambient storage recovery (%)					
0	98.1	97.2	95.6	97.4	97.8	96.0
5	97.4	93.4	91.0	92.3	91.6	95.9
15	99.6	98.8	99.5	97.1	98.5	98.7
30	95.7	92.3	94.2	92.9	93.0	94.1

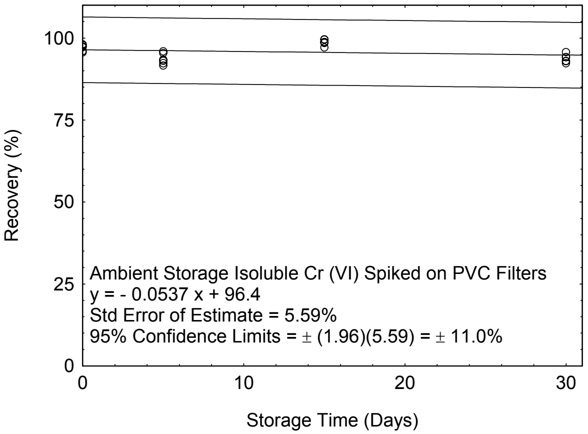

Figure 4.5.3. Ambient storage test for Insoluble Cr (VI) spiked on PVC filters.

4.6 Reproducibility

Reproducibility samples were prepared by spiking NaOHQz and PVC filters similarly as storage stability samples and then drawing 960 liters of air at 80% RH and 23 °C through them at 2 L/min. The samples were submitted to SLTC for analysis, together with a draft copy of this method. The samples were analyzed after being stored for 7 and 10 days at 23 °C for NaOHqz and PVC respectively. The reproducibility data for NaOHqz are shown in Table 4.6.1, and for PVC filters in Table 4.6.2. No sample result for Cr (VI) had a deviation greater than the precision of the overall procedure presented in Section 4.4.

Table 4.6.1
Reproducibility Data for Cr (VI)
Spiked on NaOHqz Filters

theoretical (µg/sample)	recovered (µg/sample)	recovery (%)	deviation (%)
1.0	0.983	98.3	-1.7
1.0	0.949	94.9	-5.1
1.0	0.968	96.8	-3.2
1.0	0.986	98.6	-1.4
1.0	0.959	95.9	-4.1
1.0	0.971	97.1	-2.9

Table 4.6.2
Reproducibility Data for Cr (VI)
Spiked on PVC Filters

theoretical (µg/sample)	recovered (µg/sample)	recovery (%)	deviation (%)
1.0	0.968	96.8	-3.2
1.0	0.954	95.4	-4.6
1.0	0.938	93.8	-6.2
1.0	0.945	94.5	-5.5
1.0	0.975	97.5	-2.5
1.0	0.966	96.6	-3.4

4.7 Sampler capacity

It was not possible to safely generate a test atmosphere of Cr (VI); therefore, retention efficiency tests were performed to support the recommended air volume.

4.7.1 Retention efficiency test for soluble Cr (VI) spiked on NaOHqz

A retention efficiency test for soluble Cr (VI) on NaOHqz was performed by spiking 1920 ng of Cr (VI) onto the filters, allowing them to dry, and then placing them into 37-mm polystyrene cassettes. A sampling train was constructed by placing the cassette containing the spiked NaOHqz in series with a second cassette containing a clean NaOHqz. The air flowed through the cassette containing the spiked NaOHqz and then through the second (back) cassette. These sampling trains each had 960 liters of air at

80% relative humidity at 23°C drawn through them at 2 L/min. There was no Cr (VI) found on the NaOHqz in the back cassettes.

Table 4.7.1
Retention Efficiency Test for Soluble Cr (VI) Spiked on NaOHqz

	sample number						
cassette location	1	2	3	4	5	6	mean
front NaOHqz	99.2	98.8	97.1	97.9	96.8	99.0	98.1
back NaOHqz	00.0	00.0	00.0	00.0	00.0	00.0	00.0
Total	99.2	98.8	97.1	97.9	96.8	99.0	98.1

4.7.2 Retention efficiency test for soluble Cr (VI) spiked on PVC

A retention efficiency test for soluble Cr (VI) on 37-mm PVC filters was performed as described in Section 4.7.1. There was no Cr (VI) found on the filters in the back cassettes, or on the BUPs.

Table 4.7.2.1
Retention Efficiency Test For Soluble Cr (VI) Spiked on 37-mm PVC Filters

	sample number						
cassette location	1	2	3	4	5	6	mean
front PVC	98.5	97.4	96.9	96.0	98.6	97.5	97.5
front BUP	00.0	00.0	00.0	00.0	00.0	00.0	00.0
back PVC	00.0	00.0	00.0	00.0	00.0	00.0	00.0
back BUP	00.0	00.0	00.0	00.0	00.0	00.0	00.0
Total	98.5	97.4	96.9	96.0	98.6	97.5	97.5

A retention efficiency test for soluble Cr (VI) on 25-mm PVC filters was performed as described in Section 4.7.1. There was no Cr (VI) found on the filters in the back cassettes, or on the BUPs.

Table 4.7.2.2
Retention Efficiency Test For Soluble Cr (VI) Spiked on 25-mm PVC Filters

	sample number						
cassette location	1	2	3	4	5	6	mean
front PVC	99.9	98.8	95.3	97.7	96.9	98.2	97.8
front BUP	00.0	00.0	00.0	00.0	00.0	00.0	00.0
back PVC	00.0	00.0	00.0	00.0	00.0	00.0	00.0
back BUP	00.0	00.0	00.0	00.0	00.0	00.0	00.0
total	99.9	98.8	95.3	97.7	96.9	98.2	97.8

4.8 Extraction efficiency and stability of extracted samples

4.8.1 Extraction efficiency for soluble Cr (VI) from NaOHqz

Extraction efficiency with BE/PBM

The extraction efficiency of Cr (VI) was determined by liquid-spiking NaOHqz with soluble Cr (VI) at masses ranging from 3 to 1920 ng. These samples were stored overnight at ambient temperature and then analyzed. Filters were prepared for analysis following the primary extraction procedure in sample preparation (Section 3.4). The mean extraction efficiency over the range of 3 to 1920 ng was 97.7%. Wet extraction efficiency samples were prepared by loading the filters with water by pulling 960 L of humid air (79% RH at 22 °C) through the filters at 2 L/min before spiking. The wet extraction efficiency was not included in the overall mean.

Table 4.8.1.1
Extraction Efficiency for Soluble Cr (VI) From NaOHqz
(% Recovery)

level		sample number				
× target concn	ng per sample	1	2	3	4	mean
RQL	3	96.9	99.2	97.9	97.2	97.8
0.25	240	98.9	97.4	96.4	96.4	97.3
0.5	480	98.8	97.7	99.1	96.8	98.1
1.0	960	99.2	98.2	97.1	95.7	97.6
1.5	1440	98.9	97.1	99.0	96.0	97.8
2.0	1920	98.3	96.9	97.5	98.2	97.7
1.0 (wet)	960	99.2	96.7	97.5	96.2	97.4

Stability of extracted samples

The stability of extracted samples was investigated by reanalyzing the target concentration samples 24 h after initial analysis. After the original analysis was performed, two vials were recapped with new septa while the remaining two retained their punctured septa. The samples were reanalyzed with fresh standards. The average percent change was -4.2% for samples that were resealed with new septa and -3.9% for those that retained their punctured septa. Each septum was punctured 1 time for each injection.

Table 4.8.1.2
Stability of Extracted Samples for Soluble Cr (VI) From NaOHqz

punctured septa replaced			punctured septa retained		
initial (%)	after one day (%)	difference (%)	Initial (%)	after one day (%)	difference (%)
99.2	95.3	-3.9	97.1	93.3	-3.8
98.2	93.9	-4.3	95.7	91.7	-4.0
	(mean)			(mean)	
98.7	94.6	-4.1	96.4	92.5	-3.9

4.8.2 Extraction efficiency for soluble Cr (VI) from PVC filters

Extraction efficiency with BE/PBM

The extraction efficiency of Cr (VI) was determined by liquid-spiking PVC filters with soluble Cr (VI) at masses ranging from 3 to 1920 ng. These samples were stored overnight at ambient temperature and then analyzed. Filters were prepared for analysis following the primary extraction procedure in sample preparation (Section 3.4). The mean extraction efficiency over the range of 3 to 1920 ng was 97.2%. Wet extraction efficiency samples were prepared by loading the filters with water by pulling 960 L of humid air (79% RH at 22 °C) through the filter at 2 L/min before spiking. The wet extraction efficiency was not included in the overall mean.

Table 4.8.2.1
Extraction Efficiency for Soluble Cr (VI) From PVC Filters (% Recovery)

level		sample number				
× target concn	ng per sample	1	2	3	4	mean
RQL	3	95.6	95.1	97.6	98.9	96.8
0.25	240	96.4	98.0	97.3	95.9	96.9
0.5	480	96.7	98.3	95.9	97.9	97.2
1.0	960	98.1	99.5	97.0	95.8	97.6
1.5	1440	97.8	98.5	96.8	95.3	97.1
2.0	1920	99.1	96.9	96.0	98.5	97.6
1.0 (wet)	960	98.2	97.1	96.3	96.8	97.1

Stability of extracted samples

The stability of extracted samples was investigated by reanalyzing the target concentration samples 24 h after initial analysis. After the original analysis was performed, two vials were recapped with new septa while the remaining two retained their punctured septa. The samples were reanalyzed with fresh standards. The average percent change was -3.9% for samples that were resealed with new septa and -4.5% for those that retained their punctured septa. Each septum was punctured 1 time for each injection.

Table 4.8.2.2
Stability of Extracted Samples for Soluble Cr (VI) From PVC Filters

punctured septa replaced			punctured septa retained		
initial (%)	after one day (%)	difference (%)	initial (%)	after one day (%)	difference (%)
98.1	94.0	-4.1	97.0	92.6	-4.4
99.5	95.8	-3.7	95.8	91.2	-4.6
	(mean)			(mean)	
98.8	94.9	-3.9	96.4	91.9	-4.5

4.8.3 Extraction efficiency for soluble Cr (VI) from PVC filters

Extraction efficiency with SPE/PBM

The extraction efficiency of soluble Cr (VI) was determined by liquid-spiking PVC filters with Cr (VI) at masses ranging from 3 to 1920 ng. These samples were stored overnight at ambient temperature and then analyzed. Filters were prepared for analysis following the secondary extraction procedure in sample preparation (Section 3.4). The mean extraction efficiency over the range of 3 to 1920 ng was 98.4%. Wet extraction efficiency samples were prepared by loading the filters with water by pulling 960 L of humid air (79% RH at 22 °C) through the filter at 2 L/min before spiking. The wet extraction was not included in the overall mean.

Table 4.8.3.1
Extraction Efficiency for Soluble Cr (VI) From PVC Filters
(% Recovery)

level		sample number				
× target concn	ng per sample	1	2	3	4	mean
RQL	3	97.3	98.5	99.7	97.6	98.3
0.25	240	98.9	99.1	99.3	98.0	98.8
0.5	480	99.1	97.4	98.0	98.4	98.2
1.0	960	97.9	98.8	97.6	99.2	98.4
1.5	1440	98.4	99.0	97.9	97.0	98.1
2.0	1920	99.9	97.1	98.8	99.1	98.7
1.0 (wet)	960	99.1	98.2	97.2	98.9	98.4

Stability of extracted samples

The stability of extracted samples was investigated by reanalyzing the target concentration samples 24 h after initial analysis. After the original analysis was performed, two vials were recapped with new septa while the remaining two retained their punctured septa. The samples were reanalyzed with fresh standards. The average percent change was -4.4% for samples that were resealed with new septa and -4.0% for those that retained their punctured septa. Each septum was punctured 1 time for each injection.

Table 4.8.3.2
Stability of Extracted Samples for Soluble Cr (VI) From PVC Filters

punctured septa replaced			punctured septa retained		
initial (%)	after one day (%)	difference (%)	initial (%)	after one day (%)	difference (%)
97.9	93.7	-4.2	97.6	93.8	-3.8
98.8	94.2	-4.6	99.2	95.0	-4.2
	(mean)			(mean)	
98.4	94.0	-4.4	98.4	94.4	-4.0

4.8.4 Extraction efficiency of insoluble Cr (VI) from PVC filters

Extraction efficiency with BE/PBM

The extraction efficiency of Cr (VI) was determined by liquid-spiking PVC filters with insoluble Cr (VI) at masses ranging from 3 to 1920 ng. These samples were stored overnight at ambient temperature and then analyzed. Filters were prepared for analysis following the primary extraction procedure in sample preparation (Section 3.4). The mean extraction efficiency over the range of 3 to 1920 ng was 97.7%. Wet extraction efficiency samples were prepared by loading the filters with water by pulling 960 L of humid air (79% RH at 22 °C) through the filter at 2 L/min before spiking. The wet extraction efficiency was not included in the overall mean.

Table 4.8.4.1
Extraction Efficiency for Insoluble Cr (VI) From PVC Filters
(% Recovery)

level		sample number				
× target concn	ng per sample	1	2	3	4	mean
RQL	3	94.1	96.3	97.1	98.8	96.6
0.25	240	96.6	95.3	98.2	97.6	96.9
0.5	480	97.2	96.9	98.8	97.4	97.6
1.0	960	97.8	98.4	99.1	96.9	98.0
1.5	1440	98.1	99.2	99.5	96.8	98.4
2.0	1920	98.9	99.7	99.8	97.1	98.9
1.0 (wet)	960	97.4	99.2	98.3	97.5	98.1

Stability of extracted samples

The stability of extracted samples was investigated by reanalyzing the target concentration samples 24 h after initial analysis. After the original analysis was performed, two vials were recapped with new septa while the remaining two retained their punctured septa. The samples were reanalyzed with fresh standards. The average percent change was -3.1% for samples that were resealed with new septa and -3.6% for those that retained their punctured septa. Each septum was punctured 1 time for each injection.

Table 4.8.4.2
Stability of Extracted Samples for Insoluble Cr (VI) From PVC Filters

punctured septa replaced			punctured septa retained		
initial (%)	after one day (%)	difference (%)	initial (%)	after one day (%)	difference (%)
97.8	95.1	-2.7	99.1	95.0	-4.1
98.4	94.9	-3.5	96.9	93.8	-3.1
	(mean)			(mean)	
98.1	95.0	-3.1	98.0	94.4	-3.6

4.8.5 Extraction efficiency of insoluble Cr (VI) from PVC filters

Extraction efficiency with SPE/PBM

The extraction efficiency of insoluble Cr (VI) was determined by liquid-spiking PVC filters with insoluble Cr (VI) at masses ranging from 3 to 1920 ng. These samples were stored overnight at ambient temperature and then analyzed. Filters were prepared for analysis following the secondary extraction procedure in sample preparation (Section 3.4). The mean extraction efficiency over the range of 3 to 1920 ng was 98.8%. Wet extraction efficiency samples were prepared by loading the filters with water by pulling 960 L of humid air (79% RH at 22 °C) through the filter at 2 L/min before spiking. The wet extraction efficiency was not included in the overall mean.

Table 4.8.5.1
Extraction Efficiency of Insoluble Cr (VI) From PVC Filters
(% Recovery)

level		sample number				
× target concn	ng per sample	1	2	3	4	mean
RQL	3	99.3	98.6	97.5	99.3	98.7
0.25	240	98.6	97.9	99.7	99.0	98.8
0.5	480	99.2	98.5	98.0	99.2	98.7
1.0	960	99.8	99.0	98.3	99.5	99.2
1.5	1440	99.3	98.4	99.0	97.8	98.6
2.0	1920	99.8	98.0	97.8	99.7	98.8
1.0 (wet)	960	99.6	97.9	98.8	99.2	98.9

Stability of extracted samples

The stability of extracted samples was investigated by reanalyzing the target concentration samples 24 h after initial analysis. After the original analysis was performed, two vials were recapped with new septa while the remaining two retained their punctured septa. The samples were reanalyzed with fresh standards. The average percent change was -4.4% for samples that were resealed with new septa and -3.9% for those that retained their punctured septa. Each septum was punctured 1 time for each injection.

Table 4.8.5.2
Stability of Extracted Samples for Insoluble Cr (VI) From PVC Filters

punctured septa replaced			punctured septa retained		
initial (%)	after one day (%)	difference (%)	initial (%)	after one day (%)	difference (%)
99.8	95.8	-4.0	98.3	94.7	-3.6
99.0	94.2	-4.8	99.5	95.3	-4.2
	(mean)			(mean)	
99.4	95.0	-4.4	98.9	95.0	-3.9

4.8.6 Removal efficiency of cassette wipes

The practice of wiping interior walls of filter sampling cassettes was initiated because of the following study. The interior walls of cassettes used for compliance samples received at SLTC over a three month period of time beginning in August 2000 were wiped with a PVC filter wetted with DBE/PBM.[24] The compliance samples were from three industries, chromium plating (plating), spray painting (painting), and welding (welding). Samples were analyzed within three days of the date of receipt. There was Cr (VI) found on the cassette walls of a majority of the samples. Percentages (amount on cassette walls/amount found on filter) ranged from 0-20% for plating, 3.8-13% for painting, and 0-123% for welding.

The removal efficiency of Cr (VI) from the walls of cassettes was determined by spiking the interior wall of the top piece of a 37-mm cassette with either 100 ng of $K_2Cr_2O_7$ or 100 ng of $PbCrO_4$, allowing it to dry overnight, and then wiping the cassette. Three different means of wiping the cassette were tested: wiping with a dry PVC filter, wiping with a PVC filter wetted with a drop of DI water, and wiping the cassette with a PVC filter wetted with a drop of DBE/PBM solution. There is a smooth and a rough side on a PVC filter. All wiping was performed with the rough side towards the spiked surface

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[24] Eide, M., A Study of the Deposition of Hexavalent Chromium on 37-mm Polystyrene Cassette Interior Walls, 2000, unpublished.

with a gloved hand. Filters were prepared following the primary extraction procedure in sample preparation (Section 3.4). The recoveries were similar for PVC filter wetted with a drop of DI water or DBE/PBM solution. The use of DBE/PBM solution will help eliminate interference problems, so that solution should be used for cassette wiping.

Table 4.8.6
Removal Efficiency of Cassette Wipes
(% Recovery)

sample #	dry PVC filter $K_2Cr_2O_7$	DI water PVC filter $K_2Cr_2O_7$	DBE/PBM PVC filter $K_2Cr_2O_7$	dry PVC filter $PbCrO_4$	DI water PVC filter $PbCrO_4$	DBE/PBM PVC filter $PbCrO_4$
1	87.5	97.7	98.3	79.3	86.9	88.5
2	90.2	95.6	99.9	88.6	89.4	95.8
3	88.6	94.6	95.6	86.8	88.7	93.5
4	89.5	97.1	94.9	86.5	92.8	94.9
5	86.5	96.9	97.8	92.8	91.4	92.6
6	91.2	93.9	98.3	84.6	85.9	91.4
mean	88.9	96.0	97.5	86.4	89.2	92.8

4.9 Interferences (sampling)

4.9.1 NaOHqz

Low humidity

The ability of NaOHqz to retain Cr (VI) in a relatively dry atmosphere was tested by spiking 1920 ng of Cr (VI) onto each of three filters, and placing them into polystyrene cassettes. The cassettes then had 960 liters of air with 19% RH at 24°C drawn through them at 2 L/min. All of the samples were immediately analyzed. The analytical results were 97.1%, 96.3% and 98.4% of theoretical, with a mean of 97.3%.

Low concentration

The ability of NaOHqz to retain Cr (VI) at low concentration was tested by spiking 96 ng of Cr (VI) onto each of three filters, and placing them into polystyrene cassettes. The cassettes then had 960 liters of air with 79% RH at 23°C drawn through them at 2 L/min All of the samples were immediately analyzed. The analytical results were 98.6%, 97.1% and 95.9% of theoretical, with a mean of 97.2%.

Interference

The main interferences in chromium plating operations are the acids in the baths (mainly sulfuric acid but also possibly phosphoric acid or other mineral acids) and Cr (III). The ability of NaOHqz to retain Cr (VI) in the presence of these interferences was tested by spiking 960 ng Cr (VI) onto each of three filters, along with 100 ng of Cr (III) and 50 ng of H_2SO_4 and then placing them into polystyrene cassettes. The cassettes then had 960 liters of air with 79% RH at 23°C drawn through them at 2 L/min. All of the samples were immediately analyzed. The analytical results were 98.9%, 99.7% and 99.5% of theoretical, with a mean of 99.4%.

The storage stability of Cr (VI) in the presence of H_2SO_4 was tested by spiking 27 NaOHqz with 960 ng of soluble Cr (VI) and 50 ng of H_2SO_4 and allowing the filters to dry. The spiked NaOHqz had 960 L of air with 80% RH at 23 °C drawn through them at 2 L/min. Three samples were analyzed on the day of preparation. Twelve of the filters were stored at reduced temperature (4°C) and the other twelve were stored in a closed drawer at ambient temperature (about 22°C). At 3 to 4-day intervals, three samples were selected from each of the two storage sets and analyzed. The test results show excellent storage stability.

Table 4.9.1
Storage Stability of Soluble Cr (VI) and H_2SO_4 on NaOHqz

time (days)	ambient storage recovery (%)			refrigerated storage recovery (%)		
0	98.2	99.1	96.7			
3	97.8	96.9	98.4	97.7	98.3	96.4
7	96.3	97.7	98.1	97.6	95.9	96.6
10	95.8	97.8	96.2	97.9	95.5	94.8
14	94.5	95.9	96.9	96.9	94.4	95.9

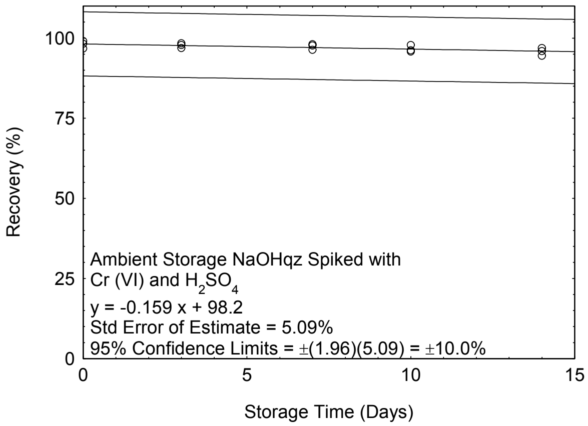

Figure 4.9.1.1. Ambient storage test for soluble Cr (VI) and H_2SO_4 spiked on NaOHqz.

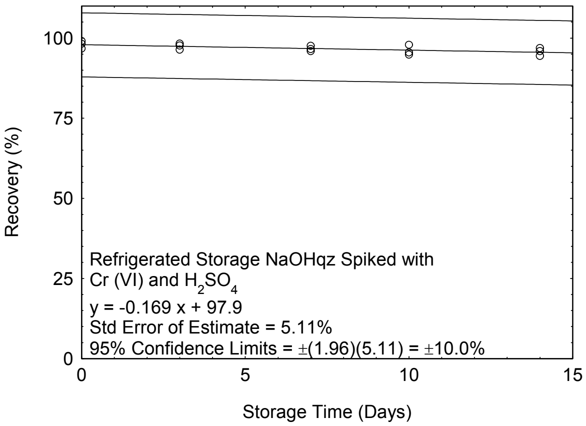

Figure 4.9.1.2. Refrigerated storage test for soluble Cr (VI) and H_2SO_4 spiked on NaOHqz.

4.9.2 PVC filter

Low humidity

The ability of PVC filters to retain Cr (VI) in a relatively dry atmosphere was tested by spiking 1920 ng of Cr (VI) onto each of three filters, and placing them into polystyrene cassettes. The cassettes then had 960 liters of air with 20% RH at 23°C drawn through them at 2 L/min. All of the samples were immediately analyzed. The analytical results were 97.8%, 99.4% and 98.1% of theoretical, with a mean of 98.4%.

Low concentration

The ability of PVC filters to retain Cr (VI) at low concentration was tested by spiking 96 ng of Cr (VI) onto each of three filters, and placing them into polystyrene cassettes. The cassettes then had 960 liters of air with 79% RH at 23°C drawn through them at 2 L/min All of the samples were immediately analyzed. The analytical results were 96.8%, 97.7% and 94.9% of theoretical, with a mean of 96.5%.

Interference

The ability of PVC filters to maintain Cr (VI) in the presence of interferences was tested several ways. Reducing metal species react with Cr (VI) changing it to Cr (III). Various ratios of Cr (VI) to Fe (II) were studied and the recoveries were 29.2, 72.5, and 91.4% for ratios of 1:10, 1:5 and 1:1, when samples were extracted with BE alone and analyzed the same day they were extracted. The Cr (VI) loading was 1000 ng. Fe (II) continued to react with Cr (VI) in BE solution, decreasing the amount of Cr (VI) recovered over time. Additionally, other reducing metals with the potential to affect recovery were tested in the following ratios and the subsequent recoveries were obtained: 1:10 Cr (VI):Mo (VI), 98.5% recovery; 1:10 Cr (VI):Mn (II), 94.4% recovery; 1:10 Cr (VI):Fe (III) 103% recovery; 1:10 Cr (VI):V (V) 103% recovery; 1:10 Cr (VI):Cu (I), 101% recovery; and 1:10 Cr (VI):Cr (III), 103% recovery. Cr (VI) loading was 1000 ng in these tests.

Magnesium (II) (from magnesium chloride) was added to the BE to precipitate reducing metal species such as Fe (II); and thereby preventing it from reacting with Cr (VI). The ratio in the above paragraph that gave the lowest results (1:10 Cr (VI):Fe (II)) was tested with Mg (II) and the recovery results improved to 92.7%. Phosphate buffer (0.5 M KH_2PO_4 0.5 M $K_2HPO_4 \cdot 3H_2O$) and $MgCl_2$ were added to 1:10 Cr (VI):Fe (II) and the recovery results improved even more to 96.6%. The precipitate using $MgCl_2$ was very fine; consequently $MgSO_4$ was tested as the source of Mg (II) and its use resulted in a larger mesh precipitate. Magnesium sulfate and phosphate buffer gave a recovery of 95.8%.

There is a positive interference from Cr (III) because it can change to Cr (VI) in an alkaline solution, in increasing amounts as alkalinity and temperature increases. SPE solution was tested for this effect because it is more alkaline than BE solution. The recovery without PBM was 104.7% for SPE extraction, and 100.6% with PBM for PVC filters spiked with 250 ng of Cr (VI) and 5 mg of Cr (III). The addition of the mixture of $MgSO_4$ and phosphate buffer (PBM) eliminated this relatively small positive interference.

The major interference in welding operations is Fe (II), which reacts with Cr (VI) to form Cr (III). Twenty-seven storage stability samples were prepared in the following manner to test this effect. A storage test was performed by spiking PVC filters with 960 ng of soluble Cr (VI) and 0.5 mg Fe (II) separately on differing spots on the same filter, and allowing the filters to dry. The dried spikes on the same filter were rubbed together to mix them. Cr (VI) and Fe (II) react slowly in the dry state but they react more quickly in a water solution to form Cr (III). For this reason, Cr (VI) and Fe (II) could not be placed in the same solution, or the solutions spiked on top of each other, but instead had to be mixed together in the dry state. The spiked PVC filters then had 960 L of air with 80% RH at 23 °C drawn through them at 2 L/min. Three samples were analyzed on the day of preparation. Twelve of the filters were stored at reduced temperature (4 °C) and the other twelve were stored in a closed drawer at ambient temperature (about 22 °C). At 3 to 4-day intervals, three samples were selected from each of the two storage sets and analyzed. Sample results were not corrected for extraction efficiency. The Evaluation Guidelines For Air Sampling Methods Utilizing Chromatographic Analysis states “A change in recovery of more than 10% in 15 days is a significant uncorrectable bias and must be avoided”.[25] The loss exceeded 10% after 7 days, showing that the samples must be analyzed within 8 days of sampling.

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[25] Evaluation Guidelines For Air Sampling Methods Utilizing Chromatographic Analysis, http://www.osha.gov/dts/sltc /methods/chromguide/index.html (accessed 11/15/03).

Table 4.9.2.1
Storage Test for Soluble Cr (VI) and Fe (II) Spiked on PVC Filters

time (days)	ambient storage recovery (%)			refrigerated storage recovery (%)		
0	98.9	96.7	97.1			
3	94.6	92.3	93.6	94.3	92.9	95.2
7	90.4	88.9	89.9	90.1	89.5	88.9
10	84.2	83.5	82.9	85.3	83.8	84.9
14	81.9	82.3	80.5	80.2	81.4	80.9

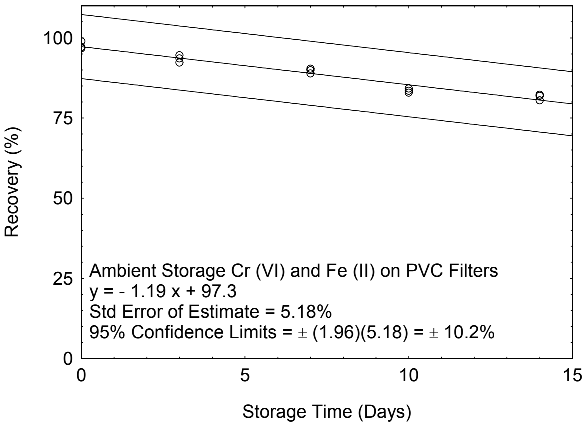

Figure 4.9.2.1 Ambient storage test for soluble Cr (VI) and Fe (II) using PVC filters.

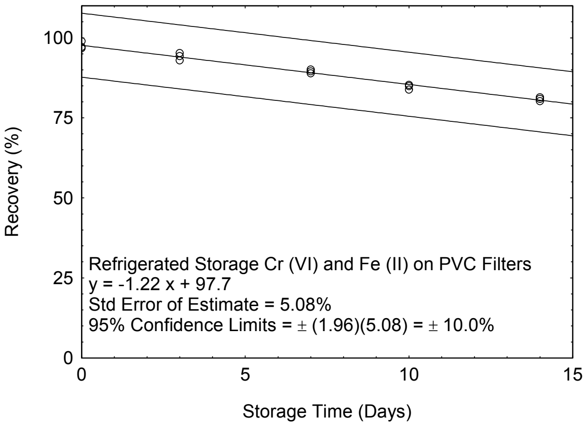

Figure 4.9.2.2 Refrigerated storage test for soluble Cr (VI) and Fe (II) using PVC filters.

The presence of acid in chrome plating operations causes a negative interference due to reaction between Cr (VI) and acid to form Cr (III). Most chrome plating baths contain H_2SO_4, accordingly a mixture of H_2SO_4 and Cr (VI) was prepared in water and used to spike PVC filters. Twenty-seven filters were each spiked with 960 ng of soluble Cr (VI) and 50 ng of H_2SO_4 and then allowed to dry. The spiked PVC filters each had 960 L air with 80% RH at 23 °C drawn through them at 2 L/min. Three samples were analyzed on the day of preparation. Twelve of the filters were stored at reduced temperature (4 °C) and the other twelve were stored in a closed drawer at ambient temperature (about 22°C). At 3 to 4-day intervals, three samples were selected from each of the two storage sets and analyzed. Sample results were not corrected for extraction efficiency. The "Evaluation Guidelines For Air Sampling Methods Utilizing Chromatographic Analysis states "A change in recovery of more than 10% in 15 days is a significant uncorrectable bias and must be avoided".[26] The loss exceeded 10% after 6 days, showing that the samples must be analyzed within 6 days of collection.

Table 4.9.2.2
Storage Test for Cr (VI) and H_2SO_4 on PVC Filters

time (days)	ambient storage recovery (%)			refrigerated storage recovery (%)		
0	98.0	96.8	97.2			
3	92.6	91.3	93.8	91.8	93.5	92.3
7	86.1	84.1	82.9	85.5	86.8	84.4
10	79.9	81.8	78.5	80.2	78.1	79.9
14	73.6	77.8	75.9	73.2	74.9	75.9

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[26] Evaluation Guidelines For Air Sampling Methods Utilizing Chromatographic Analysis, http://www.osha.gov/dts/sltc/methods/chromguide/index.html (accessed 11/15/03).

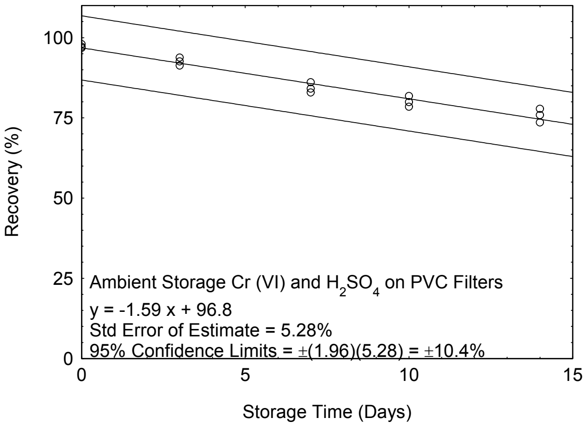

Figure 4.9.2.3 Ambient storage test for Cr (VI) and H_2SO_4 spiked on PVC filters.

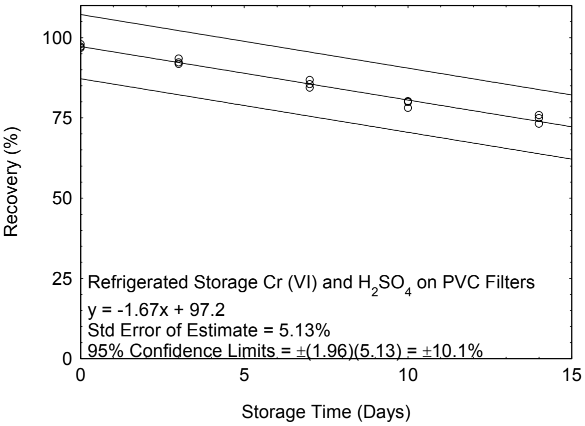

Figure 4.9.2.4 Refrigerated storage test for Cr (VI) and H_2SO_4 spiked on PVC filters.

Chromium plating samples can be stabilized by neutralizing the acid. A storage stability test was performed by placing spiked filters into BE after preparation to demonstrate this stabilization effect. The PVC filters were prepared by spiking them with 960 ng of Cr (VI) and 50 ng of H_2SO_4 and allowing them to dry before drawing 960 L of air at 80% RH and 23 °C through them at 2 L/min. The filters were placed into a vial containing 5 mL of BE immediately after drawing humid air through them. Three samples were analyzed on the day of preparation. Twelve of the filters were stored at reduced temperature (4°C) and the other twelve were stored in a closed drawer at ambient temperature (about 22°C). At 3 to 4-day intervals, three samples were selected from each of the two storage sets and analyzed. Sample results were not corrected for extraction efficiency.

Table 4.9.2.3
Storage Test for Cr (VI) and H_2SO_4 on PVC Filters and Placed Immediately in BE

time (days)		ambient storage recovery (%)			refrigerated storage recovery (%)	
0	99.1	97.9	98.1			
3	96.6	98.0	95.9	97.9	98.9	96.9
7	95.8	96.1	94.2	99.2	97.3	97.5
10	97.1	95.3	93.8	98.2	96.9	95.8
14	94.3	96.8	92.4	94.3	95.9	96.7

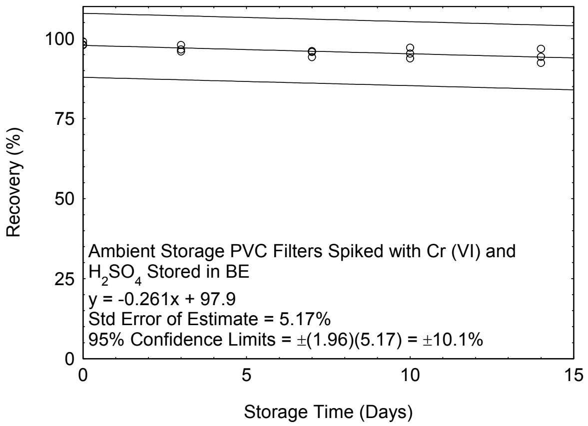

Figure 4.9.2.5. Ambient storage test for Cr (VI) and H_2SO_4 spiked on PVC filters and stored in 5 mL of BE buffer.

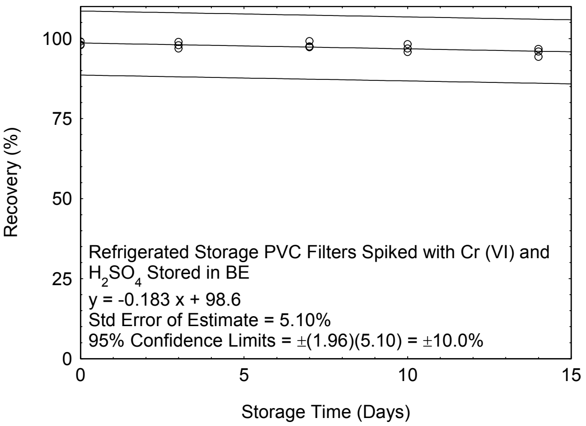

Figure 4.9.2.6 Refrigerated storage test for Cr (VI) and H_2SO_4 spiked on PVC filters and stored in 5 mL of BE buffer.

The ability of the two-step extraction process to extract Cr (VI) from a paint matrix was tested by spiking PVC filters with two drops of Sunfire 421 paint (acrylic-urethane enamel obtained from Sherwin-William Co., Cleveland, OH) and allowing the spike to dry. This paint contains lead chromate. Five samples were extracted with acid and analyzed for total chromium by ICP following OSHA Method ID-125G[27] to determine the amount of chromium in the paint so that theoretical loading on the spiked filters could be calculated. Five samples were extracted with BE/PBM, five samples were extracted with SPE/PBM, and five samples were extracted with BE/PBM followed by a second extraction with SPE/PBM. The recoveries were 46.2% for BE/PBM, 69.8% for SPE/PBM, and 101% for BE/PBM followed by SPE/PBM, illustrating that the two-step extraction is effective.

4.10 Qualitative analysis

The identity or purity of an analyte peak can be confirmed by ion chromatography using a different analytical column, such as a Dionex AS11 column. The possibility of a co-eluting species that does not react with DPC can be tested by injecting the sample with no post-column derivatizing agent added.

IC Conditions for analysis on AS11 column:

columns:	IonPac AS11 analytical column (250-mm × 4-mm i.d.) and IonPac AG-11 guard column (50-mm × 4-mm i.d.) at ambient temperature
flow rate:	1.0 mL/min
eluent:	50 mM NaOH
pump pressure:	~1000 psi
post-column derivatization solution:	~0.6 mL/min of 2.0 mM DPC in 90:10 1 N H_2SO_4:methyl alcohol
UV detector:	540 nm
injection size:	100 µL
retention time:	3.1 min
output range:	3.0 absorbance unit full scale (AUFS)

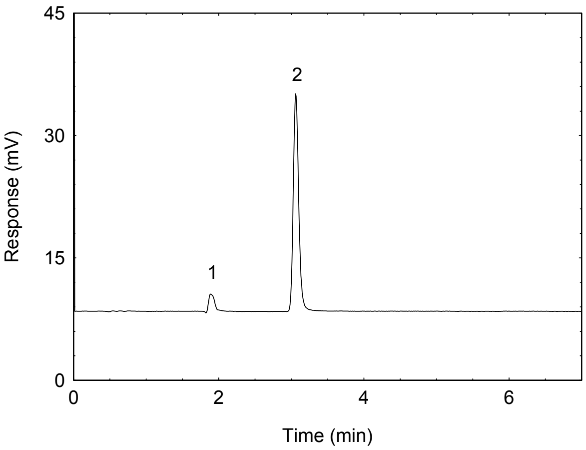

Figure 4.10. A chromatogram of 100 ng/mL Cr (VI). [Key: 1) peak in solvent, 2) Cr (VI).]

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[27] Metal and Metaloid Particulates in Workplace Atmospheres (ICP Analysis). http://www.osha.gov/dts/sltc/methods/inorganic/id125g/id125g.html (accessed 2/15/93).