

Industrial Hygiene Report  
Control of Welding Fume Particulates Using Cleanable Filter Media:

**Hexavalent Chromium**

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**Abstract**

Herein, a Sentry Air Systems product study of hexavalent chromium particles, [Cr(VI)], is reported. Due to the popularity of extended life cleanable filter media and health concerns regarding hexavalent chromium exposure in the work place, Sentry Air Systems conducted a study of the efficacy of cleanable filter systems for the maintenance of safe breathing conditions during welding operations that generate [Cr(VI)]. A Sentry Air Systems 450 Series Welding Fume Extractor was used for the containment of a representative stainless steel welding process. The collected data and analytical results suggest that the use of Sentry Air Systems 450 Series Welding Fume Extractor with MERV<sup>1</sup> 16 Micro Pleat cleanable filter media allows for safe operator breathing conditions, as shown under the conditions outlined in this paper.

**Background**

Hexavalent Chromium [Cr(VI)] — Elemental chromium is a metal component in a variety of base materials and alloys, most notably stainless steel. Whilst the metallic and low valence forms of chromium are not toxic, the hexavalent state possesses mutagenic and carcinogenic activity.<sup>2</sup> Hexavalent forms of chromium are reactive and used as an oxidizing agent in organic chemistry.<sup>3</sup> The high chromium content of stainless steel relative to other alloys, and the intense heat generated in welding, combine to provide conditions that lead to the formation of appreciable quantities of [Cr(VI)]. Vaporized metals that penetrate the welding shield gas condense upon cooling to metal oxides, including CrO<sub>3</sub>, a hexavalent form of chromium.<sup>4</sup> The carcinogenic nature of [Cr(VI)], as well as a range of chronic and acute deleterious health effects associated with exposure

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<sup>1</sup> Minimum Efficiency Reporting Value. See <https://www.ashrae.org> for information concerning MERV rating system.

<sup>2</sup> M. Cieslak-Golonka, *Polyhedron* **1996**, *15*, 3667.

<sup>3</sup> Cotton, F. A.; Wilkinson, G.; Murillo, C. A.; Bochmann, M. The Elements of the First Transition Series. In *Advanced Inorganic Chemistry*, 6<sup>th</sup> ed.; John Wiley & Sons: U.S.A., 1999.

<sup>4</sup> Fiore, S. Reducing Exposure to Hexavalent Chromium in Welding Fumes. *Welding Journal*, **2006**, 38-42.

to hexavalent chromium, has prompted regulation of this substance in the work place.<sup>5</sup> In 2006, the Occupational Safety and Health Administration (OSHA) lowered the permissible exposure limit (PEL) for [Cr(VI)] from 52 to 5 micrograms (µg) of [Cr(VI)] per cubic meter of air.<sup>6</sup> To this end, Sentry Air Systems 450 Series Welding Fume Extractors equipped with high efficiency particulate absorption (HEPA) filters have been shown to be effective for maintaining safe levels of [Cr(VI)] in worker environments.<sup>7</sup> Due to the increasing popularity of cleanable filter media in welding applications, Sentry Air Systems (SAS) sought to determine the effectiveness of our MERV 16 Micro Pleat cleanable filter media for the capture of hexavalent chromium particulates.

### **Test Design**

To test the efficacy of Sentry Air Systems cleanable filter media for capture of [Cr(VI)], a representative welding application was simulated to produce an appreciable quantity of the desired analyte. Using a Sentry Air Systems Welding Fume extractor to facilitate air filtration, air sampling was conducted to evaluate filter efficiency and air quality at multiple locations. The sampling of air at the inlet and outlet of the fume extractor system, as well as the user breathing zone and ambient room space, allows for meaningful comparisons of relevant [Cr(VI)] levels.

For this test, a continuous metal inert gas (MIG) welding operation was performed using stainless steel “coupons”. A series of parallel seams were welded lengthwise across the secured stainless steel plate, with spent coupons replaced to ensure consistent stainless steel surface interaction. The MIG weld iterations were continued for the duration of a four hour test period to generate a nearly constant fume load at the sampling source.

The sampling method was based on NIOSH Test Method 7605,<sup>8</sup> which recommends a sample volume range between 1 – 400 L and a sampling rate of 1 to 4 L/min. The guidelines were used to determine a target sample volume of 250 L, while sampling at 1.0 L/min, to ensure sufficient analyte loading for subsequent prescribed instrumental analysis.<sup>9</sup>

### **Test Equipment and Setup**

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<sup>5</sup> Occupational Safety and Health Administration.

<https://www.osha.gov/SLTC/hexavalentchromium/exposure.html> (Accessed April 28, 2014)

<sup>6</sup> Occupational Safety and Health Administration.

[https://www.osha.gov/pls/oshaweb/owadisp.show\\_document?p\\_id=12038&p\\_table=NEWS\\_RELEASES](https://www.osha.gov/pls/oshaweb/owadisp.show_document?p_id=12038&p_table=NEWS_RELEASES) (accessed April 28, 2014)

<sup>7</sup> Adams, R. F. *Control of Hexavalent Cr in Welding Fume*; Industrial Hygiene Report for Sentry Air Systems: Houston, TX, May 2007.

<sup>8</sup> National Institute for Occupational Safety and Health. This method specifically analyzes for chromium trioxide, CrO<sub>3</sub>, the most common hexavalent chromium species generated in the arc fallout. For additional details, see appended transcript of method.

<sup>9</sup> Analysis of the samples was accomplished using OSHA Method ID-215 Version 2. Consistent with NIOSH Method 7605, ion chromatography with UV-Vis detection is used in this evaluation. For additional details, see appended transcripts of the methods.

The evaluation of the filter efficiency was performed using Sentry Air Systems 450 Series Welding Fume Extractor (SS-450-WFE). The SS-450-WFE was configured with a standard carbon pre-filter pad (SS-400-CFP), and a fitted Micro Pleat Series 1 cleanable filter without previous usage or cleaning performed. The stated configuration is representative standard equipment recommended by Sentry Air Systems for most applications where particles from dust or powders are a concern. Similar to the previously reported HEPA filter system, Sentry Air Systems Micro Pleat Series 1 affects particle containment via a combination of mechanisms including interception, impaction, and diffusion.

Air sampling was conducted using SKC-branded personal air samplers (SKC-224-PCXR4), each calibrated with a BIOS International Defender 510 (Defender 510). The flow rate of each sampler was set, measured, and recorded to meet NIOSH and/or OSHA test protocol requirements. The SKC-224-PCXR4 flow rates were recorded both before and after testing and the average of the two values was used (See Table 1). Sample size was determined by using the timer onboard each SKC-224-PCXR4 air sampler along with their average calibrated flow rates.

Test design prescribed that each sampler be setup with a flow rate of about 1.0 L/min for a sample time of about 240 minutes. Following protocols of the NIOSH Method 7602, a sample train consisting of a polyvinyl chloride (PVC) filter in a polystyrene cassette filter holder were used for sample collection.<sup>10</sup> Test samples were taken at four locations during the test. Definitions of the test points can be found in the table below.

<b>Test Point A (T1A)</b>	Located at the centroid of the inlet hood face 8-12 in. from stainless steel welding surface; intake air was directed perpendicular to hood inlet, facing application.
<b>Test Point B (T1B)</b>	Located at the center of the outlet filter assembly, 1-1.5 in. below exit air stream; sampling inlet hose was directed toward the exhaust airflow.
<b>Test Point C (T1C)</b>	Located on a shelf in the working space approximately 10 feet from the test apparatus and about 6 feet off the floor.
<b>Test Point D (T1D)</b>	Located on a shirt collar of user, near the breathing zone; inlet hose directed perpendicular to weld zone-user pathway.
<b>Blank</b>	Consists of a PVC membrane from the same lot number as the other sample membranes and was subjected to the same handling procedures as the other samples, however no dynamic air sampling was performed.

At the onset of the model welding process, stainless steel coupons (~8 in. x 6 in., 316 gauge) were secured with C-clamps and seam welded using a Lincoln Electric Power MIG 215 electric welder that employed an inert gas mixture of 75% argon and 25% carbon dioxide to blanket the work.<sup>11</sup> Each coupon was exhaustively welded with sequential parallel seams across the length of the plate. Spent coupons were removed and replaced with clean, untreated stainless steel substrates, which were continuously seam-welded in identical fashion. The process was continued for the duration of the 240 minute testing period to generate a consistent fume load at the inlet of the capture hood. Visual inspection of the PVC sample membranes at the conclusion of the simulation

<sup>10</sup> PVC membrane: 5-0 µm pore size; 37 mm diameter. P/N 225-802; SKC Gulf Coast Inc. (Houston TX)

<sup>11</sup> The Safety Data Sheet (SDS) for the shielding gas mixture is appended to the manuscript.

indicated noticeable discoloration at the inlet collection location, as compared to the other testing points. The sealed samples were labeled and couriered to a third party analytical lab for testing. The laboratory analyzed the PVC membrane samplers for [Cr(VI)] content and reported the results in micrograms ( $\mu\text{g}$ ) of [Cr(VI)]. The mass data was converted to a concentration value in  $\mu\text{g}/\text{m}^3$  using the calibrated air flow sampler data (See Table 2).

### Data/Findings

Table 1. Sampling flow rate data and collected [Cr(VI)] mass.

Test Point	Sampling Time, min	Ave. Flow Rate, mL/min	% RSD Flow Rate*	Mass [Cr(VI)], $\mu\text{g}$
T1A	240	1,046.10	1.96%	4.1
T1B	240	1,056.35	0.42%	0.12
T1C	240	1,015.30	0.57%	< 0.03
T1D	240	1,050.40	1.55%	< 0.03
Blank	N/A	N/A	N/A	< 0.03

\*Percent Relative Standard Deviation of sample flow rate calculated from pre-test and post-test flow values.

Table 2. Calculated sampling volume and [Cr(VI)] concentration values.

Test Point	Sample Volume, L	[Cr(VI)], $\mu\text{g}/\text{m}^3$	[Cr(VI)], ppb*	% Filter Efficiency**
T1A	251	16	7.5	97.0%
T1B	254	0.47	0.22	
T1C	244	< 0.2	< 0.09	
T1D	252	< 0.2	< 0.09	

\*Parts per billion based on mass. \*\*Calculated from inlet and outlet [Cr(VI)] values.

### Results Summary

HIH Laboratory (Webster, TX) prepared the collected samples and measured [Cr(VI)] content using ionic chromatography analysis with UV-Vis detection (IC-UV) monitoring for the dichromate anion,  $[\text{Cr}_2\text{O}_7]^{2-}$ , a stable, water-soluble form of hexavalent chromium.<sup>12</sup> In accordance with the instrumental technique, the detection limit for  $[\text{Cr}_2\text{O}_7]^{2-}$  is 0.03  $\mu\text{g}$ , or 0.2  $\mu\text{g}/\text{m}^3$ . Therefore, for samples containing negligible quantities of  $[\text{Cr}_2\text{O}_7]^{2-}$ , a concentration less than or equal to the detection limit of IC-UV analysis is assumed.

In evaluating the efficiency of the Sentry Air Systems 450 Series Welding Fume Extractor, the detection limit of the IC-UV technique becomes an important consideration. The minimum efficiency rating, within analytical error, is 97%. Although

<sup>12</sup> Both chromate,  $[\text{CrO}_4]^{2-}$ , and dichromate,  $[\text{Cr}_2\text{O}_7]^{2-}$ , are stable salts of chromium trioxide,  $\text{CrO}_3$ . In solution, the two salts are observed in a well-defined pH dependent chemical equilibrium. Under acidic conditions, as outlined in the prescribed analytical technique, the dichromate salt is predominantly favored. See Cotton, F. A.; Wilkinson, G.; Murillo, C. A.; Bochmann, M. *The Elements of the First Transition Series*. In *Advanced Inorganic Chemistry*, 6<sup>th</sup> ed.; John Wiley & Sons: U.S.A., 1999 (pp 751-752).

the actual efficiency may be much higher, the prescribed instrumental technique limits ambient background detection to a minimal concentration of  $0.2 \mu\text{g}/\text{m}^3$ . Increasing the airborne [Cr(VI)] test load concentration, or improving the sensitivity of the instrumental technique, may result in a significantly improved efficiency rating.

Lab analysis determined  $16 \mu\text{g}/\text{m}^3$  of [Cr(VI)] at test point T1A, which corresponds to an enclosure [Cr(VI)] concentration of about  $16 \mu\text{g}/\text{m}^3$ . The concentration at the filter outlet port, T1B, reflects a total [Cr(VI)] mass of  $0.12 \mu\text{g}$  &  $0.47 \mu\text{g}/\text{m}^3$ . Based on the measured difference in concentration across the filter stack, the indicated filter efficiency for [Cr(VI)] using Sentry Air Systems MERV 16 Micro Pleat filter media is  $\geq 97\%$ . During the course of the test, the operator and room [Cr(VI)] concentration remained unchanged and below the detection limit of the IC-UV analysis.

### **Conclusions and Considerations**

The study results presented herein suggest that for the test conducted, the use of a Sentry Air Systems 450 Series Welding Fume Extractor configured with cleanable MERV 16 Micro Pleat filter media would prove beneficial in reducing operator exposure to respiratory hazards associated with welding applications. Furthermore, effective application of the aforementioned equipment for welding of chromium containing alloys may reduce operator [Cr(VI)] exposure to an acceptable sub-action level range. Under this investigation, the 97% efficiency rating of the cleanable filter media is consistent with the defined MERV 16 filter rating (95% for  $1.0\text{-}0.3 \mu\text{m}$  particles), and under the conditions of this test, the system effectively reduces [Cr(VI)] particulates to a level substantially below the OSHA & NIOSH recommended limits.<sup>13</sup>

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<sup>13</sup> NIOSH reports a recommended exposure limit (REL) for respirable [Cr(VI)] of  $0.2 \mu\text{g}/\text{m}^3$  (8 hr time-weighted average). The detection limit of IC-UV does not allow for quantifying  $\text{CrO}_3$  concentrations below  $0.2 \mu\text{g}/\text{m}^3$ . However, within experimental error, the results suggest the recommended NIOSH exposure limit is achievable under the described conditions.



Method no:	ID-215 (version 2)		
Control no.:	T-ID215-FV-02-0604-M		
Target concentration:	1.0 µg/m <sup>3</sup>		
OSHA PEL:	5.0 µg/ m <sup>3</sup> 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 <sup>3</sup> (50 µg/m <sup>3</sup> ) (water-soluble Cr (VI) compounds) 0.01 mg/m <sup>3</sup> (10 µg/m <sup>3</sup> ) (insoluble Cr (VI) compounds)		
Procedure:	<p>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.</p> <p>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.</p> <p>The filters are extracted with hot 10% Na<sub>2</sub>CO<sub>3</sub>/2% NaHCO<sub>3</sub> (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<sub>2</sub>CO<sub>3</sub> (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.</p>		
Recommended sampling time and sampling rate:	480 min at 2.0 L/min (960 L)		
Reliable quantitation limit:	NaOHqz	PVC using BE/PBM	PVC using SPE/PBM
SEE:	3.2 ng/m <sup>3</sup> 5.1%	3.5 ng/m <sup>3</sup> 5.2%	2.9 ng/m <sup>3</sup> 5.2%
Special requirements:	<p>Cr (VI) samples collected on PVC filters must be shipped overnight to OSHA Salt Lake Technical Center (SLTC) within 24 hours of sampling.</p> <p>Cr (VI) samples collected on PVC filters from welding operations must be analyzed within 8 days of sampling (Section 4.5.6).</p> <p>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.</p>		
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	James C. Ku, Mary Eide		

Methods Development Team  
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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<sup>1</sup> 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<sup>2</sup>. Therefore, a new method (OSHA ID-215<sup>3</sup>) 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<sup>4</sup> 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<sup>5</sup>, 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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<sup>1</sup> Ku, J., Hexavalent Chromium ID-103, <http://www.osha.gov/dts/sltc/methods/inorganic/id103/id103.html> (accessed 11/2/04).

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

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

<sup>4</sup> 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.

<sup>5</sup> Puskar, M.A., Harkins, J.M., Moomey, J.D., Hecker, L.H., Internal Wall Losses of Pharmaceutical 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.<sup>6</sup>

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.<sup>7</sup> 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.<sup>8</sup> 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.)<sup>9</sup>

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

<sup>6</sup> Eide, M., A Study of the Iron (II) Interference in Samples Requesting Analysis for Hexavalent Chromium, 2002, unpublished.

<sup>7</sup> 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.

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

<sup>9</sup> 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<sup>10,11</sup>

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))<sup>12</sup>: 0689

IMIS number used prior to 5/30/2006 (Chromic acid and Chromates (as CrO<sub>3</sub>))<sup>13</sup>: 0686

#### chromium trioxide<sup>14</sup>

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<sub>3</sub> solubility: very sol in water, insol in alcohol

#### lead chromate<sup>15</sup>

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<sub>4</sub> solubility: very slightly sol in water, sol in strong acids and alkalis

#### potassium chromate<sup>16</sup>

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<sub>2</sub>CrO<sub>4</sub> solubility: sol in water, insol in alcohol

#### potassium dichromate<sup>17</sup>

synonyms: potassium bichromate

<sup>10</sup> Occupational Exposure to Hexavalent Chromium- 71 FR at 10104, [www.osha.gov/pls/oshaweb/owadispl.show\\_document?p\\_table=FEDERAL\\_REGISTER&p\\_id=18599](http://www.osha.gov/pls/oshaweb/owadispl.show_document?p_table=FEDERAL_REGISTER&p_id=18599) (accessed 2/28/06).

<sup>11</sup> *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.

<sup>12</sup> OSHA Chemical Sampling Information. [http://www.osha.gov/dts/chemicalsampling/data/CH\\_228697.html](http://www.osha.gov/dts/chemicalsampling/data/CH_228697.html) (accessed 7/10/2006).

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

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

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

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

<sup>17</sup> O'Neil, M.J., Sr. Ed., *The Merck Index*, 13<sup>th</sup> 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<sup>18</sup>

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

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This method was evaluated according to the OSHA SLTC "Evaluation Guidelines for Air Sampling Methods Utilizing Chromatographic Analysis"<sup>19</sup>. 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.

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## 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<sup>3</sup>) for Cr (VI) on NaOHqz, 1.00 ng/sample (1.0 ng/m<sup>3</sup>) for Cr (VI) on PVC filters extracted with BE/PBM, and 0.80 ng/sample (0.83 ng/m<sup>3</sup>) 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<sup>3</sup>) for Cr (VI) on NaOHqz, 3.33 ng/sample (3.5 ng/m<sup>3</sup>) for Cr (VI) on PVC filters extracted with BE/PBM, and 2.67ng/sample (2.9 ng/m<sup>3</sup>) 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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<sup>18</sup> Lewis, R.J. Sr., Ed., *Hazardous Chemicals Desk Reference*, Van Nostrand Reinhold, New York, 1997, p 1240.

<sup>19</sup> 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  $\pm 9.92\%$  and the precision for PVC filters was  $\pm 10.0\%$ . 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  $\pm 5\%$  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  $\mu\text{g}$  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- $\mu\text{m}$  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- $\mu$ m 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- $\mu$ m 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%  $\pm$ 3.5% has been reported for chromic acid mist collected on PVC filters by other researchers<sup>20</sup>.

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<sup>20</sup> Dutkiewicz, R., Konczalik, J., Przechera, M., Assessment 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<sub>2</sub>SO<sub>4</sub>, 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<sub>2</sub>SO<sub>4</sub> 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".<sup>21</sup> 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<sub>2</sub>SO<sub>4</sub>, so a mixture of H<sub>2</sub>SO<sub>4</sub> 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<sub>2</sub>SO<sub>4</sub> 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<sup>22</sup>. Avoid skin contact and inhalation of all chemicals and review all MSDSs before beginning this analytical procedure.

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

<sup>22</sup> Occupational Exposure to Hazardous Chemicals in Laboratories, [http://www.osha.gov/pls/oshaweb/owadisp.show\\_document?p\\_table=STANDARDS&p\\_id=10106](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<sup>32</sup> 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%  $\text{NH}_4\text{OH}$  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%  $\text{NaHCO}_3$  with 10%  $\text{Na}_2\text{CO}_3$ ): Place about 500 mL of DI water in a 1-L volumetric flask, add 20 g of  $\text{NaHCO}_3$ , swirl to dissolve, then add 100 g of  $\text{Na}_2\text{CO}_3$ , 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%  $\text{NaOH}$  + 7.5%  $\text{Na}_2\text{CO}_3$ ): Dissolve 50 g of  $\text{NaOH}$  and 75 g of  $\text{Na}_2\text{CO}_3$  in about 500 mL of DI  $\text{H}_2\text{O}$  contained in a 1.0-L volumetric flask. Allow the solution to cool to room temperature, and then dilute to the mark with DI  $\text{H}_2\text{O}$ . 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  $\text{KH}_2\text{PO}_4$  with 0.5 M  $\text{K}_2\text{HPO}_4 \cdot 3\text{H}_2\text{O}$ ): Place about 500 mL of DI water in a 1-L volumetric flask, add 68 g of  $\text{KH}_2\text{PO}_4$  and 114 g of  $\text{K}_2\text{HPO}_4 \cdot 3\text{H}_2\text{O}$ , swirl to dissolve and dilute up to the mark with DI water.

Phosphate buffer/ $\text{MgSO}_4$  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/ $\text{MgSO}_4$  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  $(\text{NH}_4)_2\text{SO}_4$  with 100 mM  $\text{NH}_4\text{OH}$ ]: 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  $\text{H}_2\text{SO}_4$ :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  $\mu\text{g}/\text{mL}$  of Cr (VI) by dissolving approximately 0.2828 g of  $\text{K}_2\text{Cr}_2\text{O}_7$  in 1.000 L of DI water. (For example: the calculation for a stock standard is:  $(0.2828 \text{ g } \text{K}_2\text{Cr}_2\text{O}_7/\text{liter}) \times (1000 \text{ mg/g}) \times (1000 \text{ } \mu\text{g}/\text{mg}) \times (\text{L}/1000 \text{ mL}) \times (\text{MW Cr}/\text{MW } \text{K}_2\text{Cr}_2\text{O}_7) = 51.996/294.18) \times (2 \text{ moles of Cr in } \text{K}_2\text{Cr}_2\text{O}_7) = 100 \text{ } \mu\text{g}/\text{mL Cr (VI).)$  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  $\text{ng}/\text{mL}$ . 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  $^{\circ}\text{C}$  which is below the boiling point of BE solution. A hot water bath set at 100  $^{\circ}\text{C}$  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 °C 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 °C 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<sub>4</sub>)<sub>2</sub>SO<sub>4</sub> with 100 mM NH<sub>4</sub>OH  
pump pressure: ~1200 psi  
post-column derivatization solution: ~0.6 mL/min of 2.0 mM DPC in 90:10 1 N H<sub>2</sub>SO<sub>4</sub>:methyl alcohol  
UV detector: 540 nm  
injection size: 100 µL  
retention time: 5.3 min  
output range: 0.1 absorbance unit full scale (AUFS)

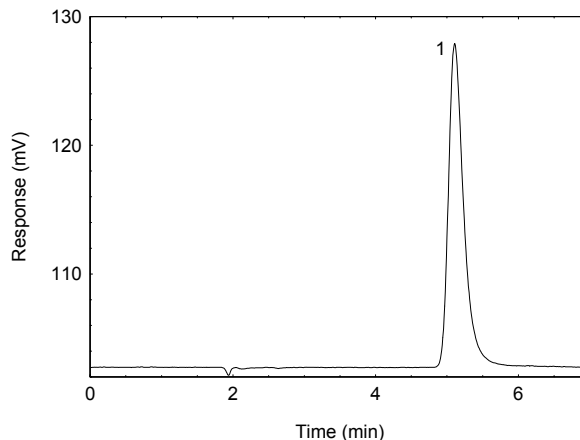


Figure 3.5.1. A chromatogram of 100 ng/mL Cr (VI). [Key: 1) Cr (VI).]

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.

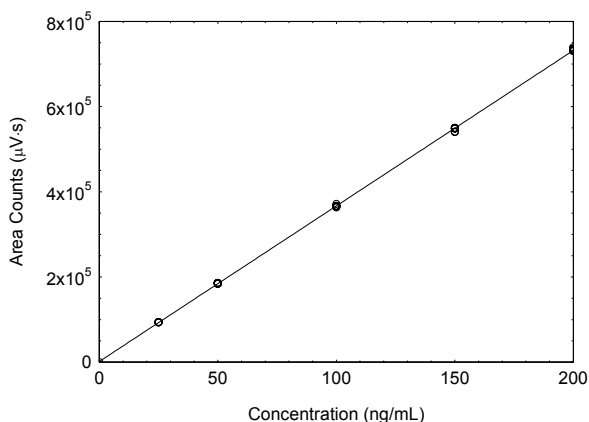


Figure 3.5.2. Calibration curve of Cr (VI). ( $y = 3650x + 1901$ )

### 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:

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

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:

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

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:

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

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)
$Cr (VI)_{CBE/PBMbik}$	= 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

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

$Cr (VI)_{CSPE/PBM}$	= 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)
$Cr (VI)_{CSPE/PBMbik}$	= 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"<sup>23</sup>. 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<sup>32</sup> 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.

<sup>23</sup> 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 ( $\mu\text{V}\cdot\text{s}$ )
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

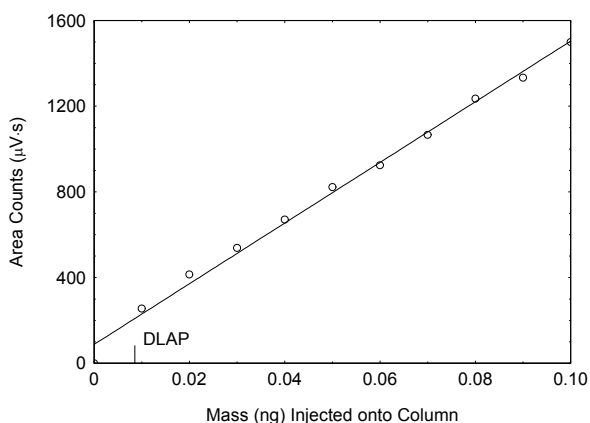


Figure 4.1. Plot of data to determine the DLAP. ( $y = 1.42\text{E}4x + 87.8$ )

#### 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 ( $0.94 \text{ ng/m}^3$ ). 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 ( $1.0 \text{ ng/m}^3$ ). 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 ( $1.0 \text{ ng/m}^3$ ).

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

mass per sample (ng)	area counts ( $\mu\text{V}\cdot\text{s}$ )
0	0
1	245
2	408
3	534
4	667
5	786
6	897
7	1011
8	1234
9	1324
10	1439

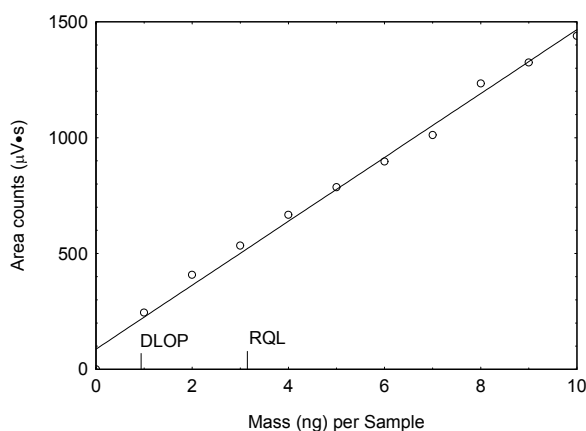


Figure 4.2.1. Plot of data in Table 4.2.1 used to determine the DLOP/RQL for NaOHqz extracted with BE/PBM. ( $y = 138x + 87.1$ )

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

mass per sample (ng)	area counts ( $\mu\text{V}\cdot\text{s}$ )
0	0
1	237
2	389
3	504
4	657
5	751
6	865
7	971
8	1170
9	1243
10	1395

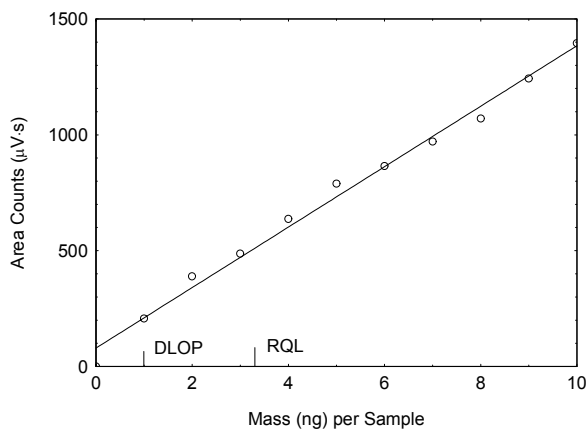


Figure 4.2.2. Plot of data in Table 4.2.2 used to determine the DLOP/RQL for PVC filters extracted with BE/PBM. ( $y = 131x + 79.5$ )

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

mass per sample (ng)	area counts ( $\mu\text{V}\cdot\text{s}$ )
0	0
1	211
2	379
3	459
4	601
5	783
6	899
7	980
8	1188
9	1256
10	1410

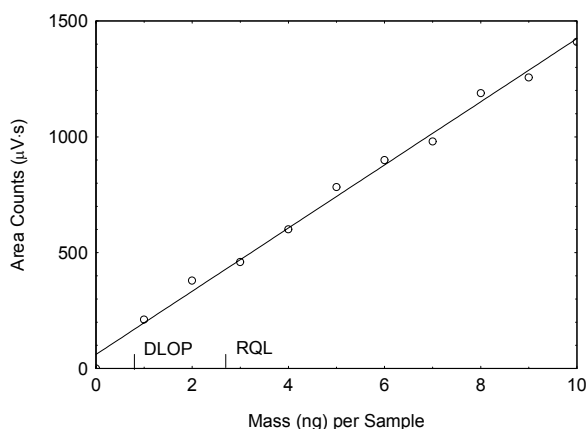


Figure 4.2.3. Plot of data in Table 4.2.3 used to determine the DLOP/RQL for PVC filters extracted with SPE/PBM. ( $y = 136x + 60.7$ )

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 ( $3.2 \text{ ng}/\text{m}^3$ ). Recovery at this concentration is 97.8%. The RQL for PVC filters extracted with BE/PBM is 3.32 ng per sample ( $3.5 \text{ ng}/\text{m}^3$ ), and 2.67 ng per sample ( $2.9 \text{ ng}/\text{m}^3$ ) 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.



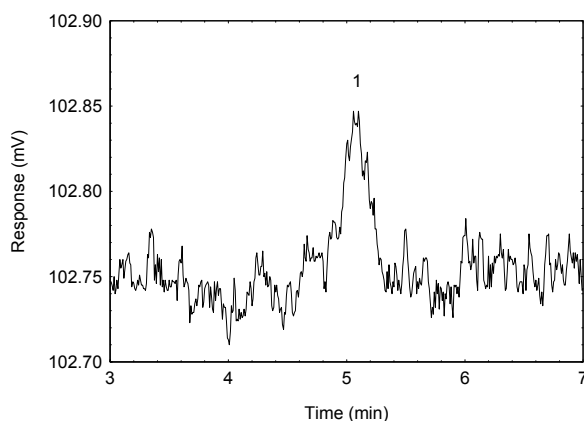


Figure 4.2.4 A chromatogram of a standard near the RQL. Key: 1 = Cr (VI).

#### 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 ( $\mu\text{V}\cdot\text{s}$ )					
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  $\pm 9.92\%$  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  $\pm 10.0\%$  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  $\pm 5\%$  for sampling error.

#### 4.5 Storage tests

Soluble Cr (VI) is defined as Cr (VI) from  $\text{K}_2\text{Cr}_2\text{O}_7$  dissolved in DI water; and insoluble Cr (VI) as Cr (VI) from  $\text{PbCrO}_4$  dissolved in BE solution. Lead chromate ( $\text{PbCrO}_4$ ) 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

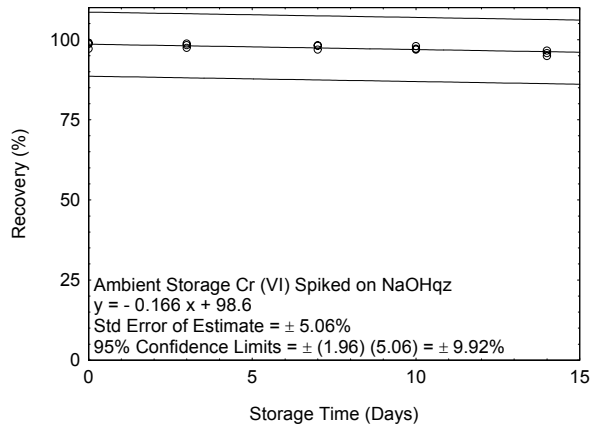


Figure 4.5.1.1. Ambient storage test for soluble Cr (VI) spiked on NaOHqz.

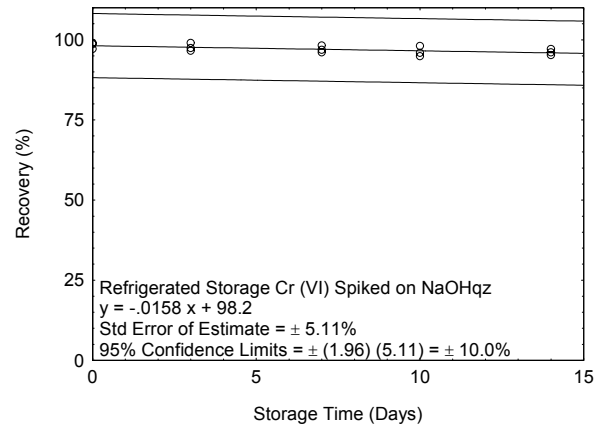


Figure 4.5.1.2. Refrigerated storage test for soluble Cr (VI) spiked on NaOHqz.

#### 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	96.7	97.4
5	96.9	95.9	96.0	97.1	98.8	95.1
10	95.8	96.9	96.7	95.2	96.4	97.3
15	97.8	97.6	94.5			

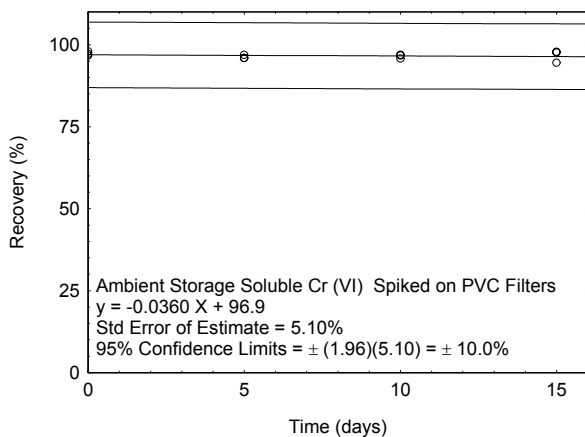


Figure 4.5.2.1. Ambient storage test for soluble Cr (VI) spiked on PVC filters.

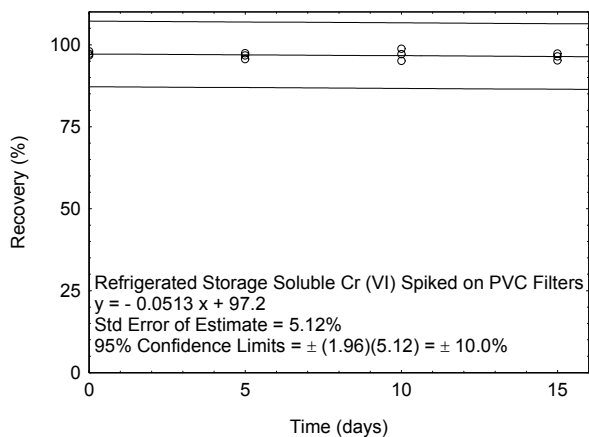


Figure 4.5.2.2. Refrigerated storage test for soluble Cr (VI) spiked on PVC filters.

#### 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
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

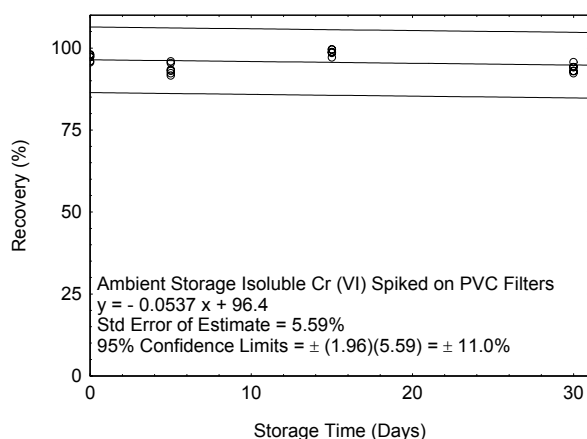


Figure 4.5.3. Ambient storage test for Insoluble Cr (VI) spiked on PVC filters.

#### 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 ( $\mu\text{g}/\text{sample}$ )	recovered ( $\mu\text{g}/\text{sample}$ )	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 ( $\mu\text{g}/\text{sample}$ )	recovered ( $\mu\text{g}/\text{sample}$ )	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

cassette location	<u>sample number</u>						mean
	1	2	3	4	5	6	
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

cassette location	<u>sample number</u>						mean
	1	2	3	4	5	6	
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

cassette location	<u>sample number</u>						mean
	1	2	3	4	5	6	
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)

× target concn	level		sample number				mean
	ng per sample		1	2	3	4	
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)

× target concn	level		sample number				mean
	ng per sample		1	2	3	4	
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)

× target concn	level		sample number				mean
	ng per sample		1	2	3	4	
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)

× target concn	level		sample number				mean
	ng per sample		1	2	3	4	
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)

× target concn	level		sample number				mean
	ng per sample		1	2	3	4	
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.<sup>24</sup> 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<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub> or 100 ng of PbCrO<sub>4</sub>, 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

<sup>24</sup> 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 <sub>2</sub> Cr <sub>2</sub> O <sub>7</sub>	DI water PVC filter K <sub>2</sub> Cr <sub>2</sub> O <sub>7</sub>	DBE/PBM PVC filter K <sub>2</sub> Cr <sub>2</sub> O <sub>7</sub>	dry PVC filter PbCrO <sub>4</sub>	DI water PVC filter PbCrO <sub>4</sub>	DBE/PBM PVC filter PbCrO <sub>4</sub>
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<sub>2</sub>SO<sub>4</sub> 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<sub>2</sub>SO<sub>4</sub> was tested by spiking 27 NaOHqz with 960 ng of soluble Cr (VI) and 50 ng of H<sub>2</sub>SO<sub>4</sub> 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<sub>2</sub>SO<sub>4</sub> 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

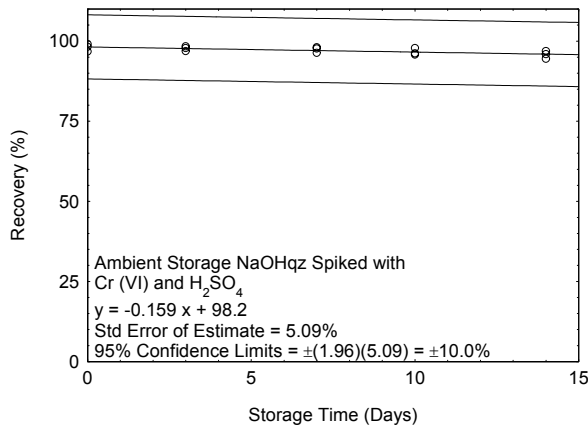


Figure 4.9.1.1. Ambient storage test for soluble Cr (VI) and H<sub>2</sub>SO<sub>4</sub> spiked on NaOHqz.

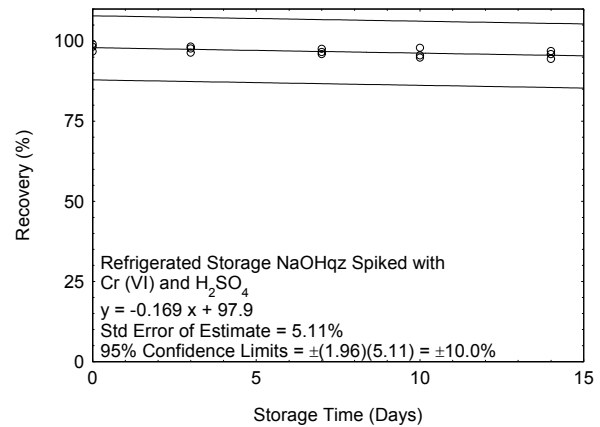


Figure 4.9.1.2. Refrigerated storage test for soluble Cr (VI) and H<sub>2</sub>SO<sub>4</sub> spiked on NaOHqz.

#### 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  $\text{KH}_2\text{PO}_4$  0.5 M  $\text{K}_2\text{HPO}_4 \cdot 3\text{H}_2\text{O}$ ) and  $\text{MgCl}_2$  were added to 1:10 Cr (VI):Fe (II) and the recovery results improved even more to 96.6%. The precipitate using  $\text{MgCl}_2$  was very fine; consequently  $\text{MgSO}_4$  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  $\text{MgSO}_4$  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".<sup>25</sup> The loss exceeded 10% after 7 days, showing that the samples must be analyzed within 8 days of sampling.

<sup>25</sup> 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	94.3	92.9
3	94.6	92.3	93.6	90.1	89.5	88.9
7	90.4	88.9	89.9	85.3	83.8	84.9
10	84.2	83.5	82.9	80.2	81.4	80.9
14	81.9	82.3	80.5			

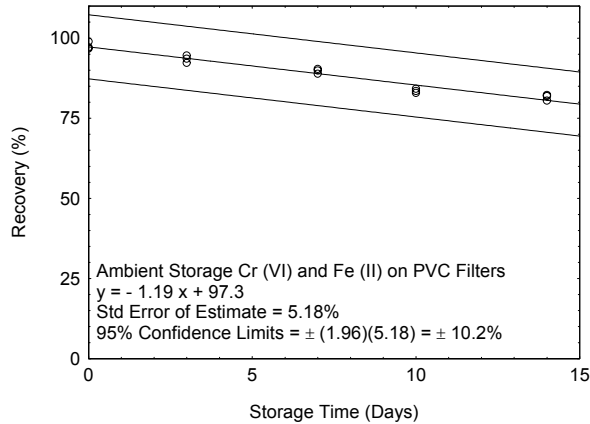


Figure 4.9.2.1 Ambient storage test for soluble Cr (VI) and Fe (II) using PVC filters.

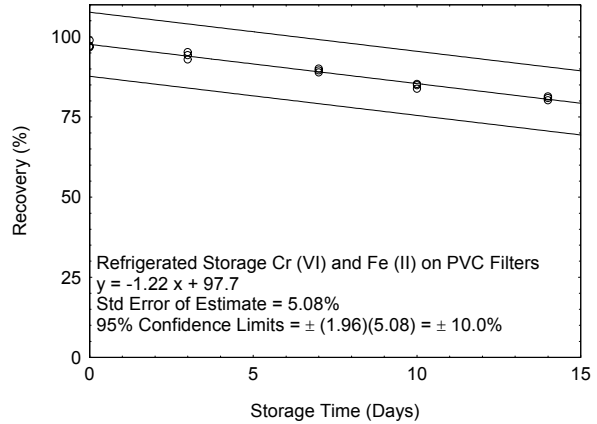


Figure 4.9.2.2 Refrigerated storage test for soluble Cr (VI) and Fe (II) using PVC filters.

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<sub>2</sub>SO<sub>4</sub>, accordingly a mixture of H<sub>2</sub>SO<sub>4</sub> 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<sub>2</sub>SO<sub>4</sub> 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".<sup>26</sup> 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<sub>2</sub>SO<sub>4</sub> 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

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

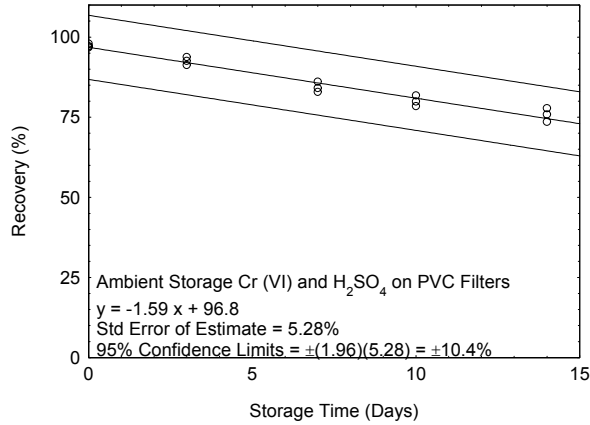


Figure 4.9.2.3 Ambient storage test for Cr (VI) and H<sub>2</sub>SO<sub>4</sub> spiked on PVC filters.

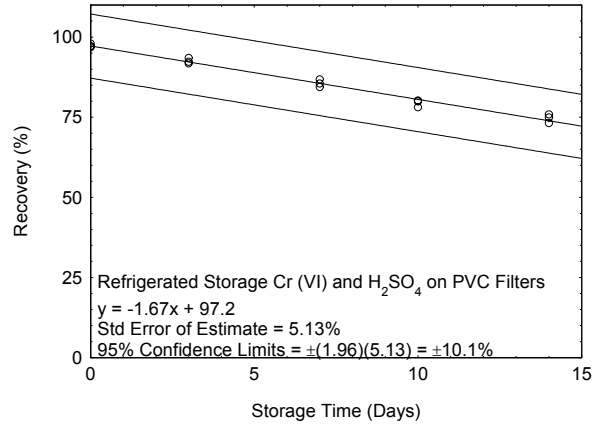


Figure 4.9.2.4 Refrigerated storage test for Cr (VI) and H<sub>2</sub>SO<sub>4</sub> spiked on PVC filters.

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<sub>2</sub>SO<sub>4</sub> 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<sub>2</sub>SO<sub>4</sub> 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
7	95.8	96.1	94.2	99.2	97.3
10	97.1	95.3	93.8	98.2	96.9
14	94.3	96.8	92.4	94.3	95.9

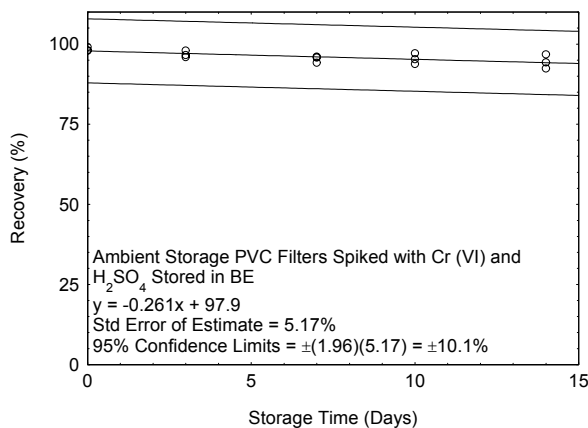


Figure 4.9.2.5. Ambient storage test for Cr (VI) and H<sub>2</sub>SO<sub>4</sub> spiked on PVC filters and stored in 5 mL of BE buffer.

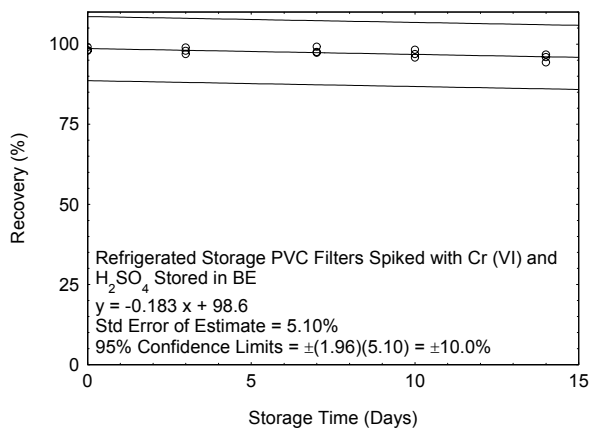


Figure 4.9.2.6 Refrigerated storage test for Cr (VI) and H<sub>2</sub>SO<sub>4</sub> spiked on PVC filters and stored in 5 mL of BE buffer.

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<sup>27</sup> 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 <sub>2</sub> SO <sub>4</sub> :methyl alcohol
UV detector:	540 nm
injection size:	100 µL
retention time:	3.1 min
output range:	3.0 absorbance unit full scale (AUFS)

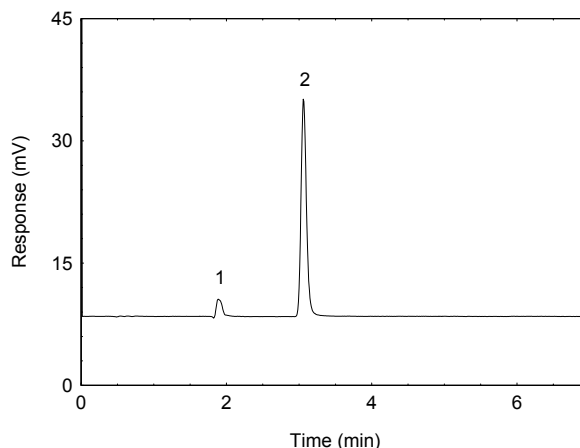


Figure 4.10. A chromatogram of 100 ng/mL Cr (VI). [Key: 1) peak in solvent, 2) Cr (VI).]

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



# CHROMIUM, HEXAVALENT by Ion Chromatography

7605

Cr(VI)      MW: 52.00 (Cr); 99.99 (CrO<sub>3</sub>)      CAS: 18540-29-9      RTECS: GB6262000

**METHOD:** 7605, Issue 1

**EVALUATION:** FULL

**Issue 1:** 15 March 2003

**OSHA :** 0.1 mg/m<sup>3</sup> (as CrO<sub>3</sub>)  
**NIOSH:** 0.001 mg/m<sup>3</sup>/10 h; carcinogen  
**ACGIH:** 0.050 mg/m<sup>3</sup> (as Cr, soluble); some insoluble chromates are human carcinogens

**PROPERTIES:** oxidizing agent

**SYNONYMS:** Vary depending upon the compound; chromate commonly used, "chrome six."

SAMPLING		MEASUREMENT	
<p><b>SAMPLER:</b> FILTER (5.0-<math>\mu</math>m PVC membrane)</p> <p><b>FLOW RATE:</b> 1 to 4 L/min</p> <p><b>VOL-MIN:</b> 1 L @ 0.05 mg/m<sup>3</sup>  <b>-MAX:</b> 400 L</p> <p><b>SHIPMENT:</b> Routine. Can be shipped cold when deemed necessary.</p> <p><b>SAMPLE STABILITY:</b> Stable for 2 weeks at room temperature. Stable for 4 weeks if stored in refrigerator.</p> <p><b>BLANKS:</b> 2 to 10 field blanks per set</p>	<p><b>TECHNIQUE:</b> Ion chromatography with post-column derivatization and UV detection.</p> <p><b>ANALYTE:</b> CrO<sub>4</sub><sup>-2</sup>-diphenylcarbazide (DPC) complex</p> <p><b>EXTRACTION:</b> 5 mL 2% NaOH- 3% Na<sub>2</sub>CO<sub>3</sub>. Dilute to 25 mL after heating.</p> <p><b>INJECTION VOLUME:</b> 100 <math>\mu</math>L</p> <p><b>COLUMN:</b> Dionex NG1 Guard, HPIC- AS7 Separator or equivalent</p> <p><b>MOBILE PHASE:</b> 250 mM (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub> /100 mM NH<sub>4</sub>OH</p> <p><b>FLOW RATE:</b> 1.0 mL/min; 0.7 mL/min post column</p> <p><b>POST-COLUMN REAGENT:</b> 2.0 mM DPC + 10% MeOH +1N H<sub>2</sub>SO<sub>4</sub></p> <p><b>DETECTOR:</b> 540 nm</p> <p><b>CALIBRATION:</b> Standard solutions of K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub> in NaOH-Na<sub>2</sub>CO<sub>3</sub> buffer</p> <p><b>RANGE:</b> 0.05 to 20 <math>\mu</math>g per sample</p> <p><b>ESTIMATED LOD:</b> 0.02 <math>\mu</math>g per sample [3]</p> <p><b>PRECISION (<math>\hat{S}_r</math>):</b> 0.015 @ 0.5 to 5 <math>\mu</math>g/sample [3]</p>		
ACCURACY			
<p><b>RANGE STUDIED:</b> 0.05 to 120 <math>\mu</math>g Cr(VI) [1,2]</p> <p><b>BIAS:</b> -1.6% [2]</p> <p><b>OVERALL PRECISION (<math>\hat{S}_{rT}</math>):</b> 0.07</p> <p><b>ACCURACY:</b> <math>\pm</math> 17.4% (0.6 - 960 <math>\mu</math>g/m<sup>3</sup>) [1]</p>			

**APPLICABILITY:** The working range is 0.00025 to 0.1 mg/m<sup>3</sup> for a 200-L air sample. This method can be used for the determination of Cr(VI) using 2% NaOH - 3% Na<sub>2</sub>CO<sub>3</sub> for extraction.

**INTERFERENCES:** Possible interferences are iron, copper, nickel, and vanadium; 10  $\mu$ g of any of these causes an absorbance equivalent to approximately 0.02  $\mu$ g Cr(VI) due to formation of colored complexes. Interference due to reducing agents (e.g., Fe, Fe++) is minimized by alkaline extraction (step 5).

**OTHER METHODS:** Method 7703 is a field portable method for Cr(VI). OSHA Method W4001 is for the measurement of Cr(VI) in wipe samples [4]. OSHA Method ID-215 is for measurement of Cr(VI) and employs precipitation to reduce Cr(III) oxidation. [5]. A similar air method is ISO 16740 [6]. EPA Method 218.6 is for water matrices [7]. Method 7604 is also specific for hexavalent chromium, using ion chromatography, but has a higher detection limit than 7605.

**REAGENTS:**

1. Sulfuric acid, conc. (98% w/w).\*
2. Ammonium hydroxide, conc. (28%).\*
3. Ammonium sulfate monohydrate, reagent grade.
4. Sodium carbonate, anhydrous.
5. Sodium hydroxide, reagent grade.\*
6. Methanol, HPLC grade.\*
7. 1,5-Diphenylcarbazide, reagent grade.
8. Potassium dichromate or potassium chromate.\* Dry at 100 °C and store in a desiccator.
9. Post-Column Derivatizing Reagent:  
Diphenylcarbazide solution. Dissolve 500 mg 1,5-diphenylcarbazide in 100 mL HPLC-grade methanol. While stirring, add 500 mL water containing 28 mL of conc. sulfuric acid. Dilute to a final volume of one liter with water. This reagent is stable for 4 - 5 days. Prepare in one-liter quantities as needed.
10. Cr(VI) standard, 1000 µg/mL. Dissolve 2.829 g potassium dichromate in deionized water to make one liter, or use commercially available solution.  
NOTE: 3.731 g  $K_2CrO_4$  can also be used.
11. Calibration stock solution, 1.0 µg/mL. Dilute 1000 µg/mL Cr(VI) standard 1:1000 with deionized water.
12. Filter extraction solution, 2% NaOH-3%  $Na_2CO_3$ . Dissolve 20 g NaOH and 30 g  $Na_2CO_3$  in deionized water to make one liter of solution.
13. Eluent (mobile phase); 250 mM ammonium sulfate/200 mM ammonium hydroxide. Dissolve 33 g ammonium sulfate in approximately 500 mL distilled water and add 6.5 mL conc. ammonium hydroxide. Dilute to one liter with distilled water and mix.
14. Nitrogen, pre-purified.

\* See SPECIAL PRECAUTIONS

**EQUIPMENT:**

1. Sampler: polyvinyl chloride (PVC) filter, 5.0-µm pore size, 37-mm diameter in polystyrene cassette filter holder.  
NOTE: Some PVC filters promote reduction of Cr(VI). Check each lot of filters for recovery of Cr(VI) standard.
2. Personal sampling pump, 1 to 4 L/min, with flexible connecting tubing.
3. Vials, scintillation, 20-mL glass, PTFE-lined screw cap.\*\*
4. Forceps, nonmetallic.
5. Gloves, polypropylene or latex.
6. Liquid chromatography apparatus consisting of autosampler; pump; NG1 (Dionex Corp.) or equivalent guard column; HPIC-AS7, 4 x 250-mm (Dionex Corp.) separator column (or equivalent); post-column reagent delivery system, 2.2-m PEEK™ tubing mixing/reaction loop with 1 m in a water bath at 32 °C ± 3 °C; and UV detector.
7. Filtration apparatus, PTFE luer-lock filter (Gelman IC Acrodisc or equivalent)/syringe.
8. Beakers, borosilicate, 50-mL.\*\*
9. Watch glass.\*\*
10. Volumetric flasks, 25-, 100-, and 1000-mL.\*\*
11. Oven at 107°C, not to exceed 115°C.  
NOTE: Hot plate can be used. An ultrasonic bath can be used instead of oven or hot plate.
12. Micropipettes, 10-µL to 0.5-mL.
13. Pipettes, TD 5-mL.\*\*
14. Bagged refrigerant.

\*\* Clean all glassware with 1:1  $HNO_3:H_2O$  and rinse thoroughly before use.

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**SPECIAL PRECAUTIONS:** Many chromate compounds are suspected human carcinogens [8]. All sample preparation should be performed in a hood. Concentrated acids and bases are toxic and corrosive. When working with concentrated acids and bases, wear protective clothing. Ammonium hydroxide is a respiratory irritant. Methanol is flammable and toxic.

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**SAMPLING:**

1. Calibrate the sampling pump with a representative sampler in line.
2. Sample at an accurately known flow rate in the range 1 to 4 L/min for a sample size of 1 to 400 L. Do not exceed 1 mg total dust loading on the filter.

3. Filters can be left in the cassettes for shipping to the lab, but to minimize sample contamination during shipping, remove the filter from the cassette within one hour of completion of sampling and place it in a vial to be shipped to the laboratory. Handle the filter only with gloved hands and nonmetallic forceps. Discard the backup pad. As a precaution, it is recommended to ship the samples with bagged refrigerant.

#### **SAMPLE PREPARATION:**

4. Don a clean pair of disposable plastic gloves (to prevent sample contamination). Using forceps, transfer the PVC filter to a 50-mL beaker, and add 5.0 mL filter extraction solution, 2% NaOH/3% Na<sub>2</sub>CO<sub>3</sub>. Start media blanks at this point.

NOTE 1: If significant amounts of Cr[III] are expected to be present in the samples, either (a) degas the sodium hydroxide/sodium carbonate extraction solution by bubbling nitrogen through it for 5 min. before proceeding, or (b) use a precipitation reagent [1].

NOTE 2: If only soluble chromates are of interest, use ammonium sulfate buffer in place of carbonate extraction solution [9, 10].

5. Cover the beaker with a watchglass and heat it to near the boiling point (100°C to 115°C) in an oven with occasional swirling for 45 min. Do not boil the solution. Longer heating times (up to 90 minutes) may be necessary for some samples (e.g., paint spray). Do not allow the solution to evaporate to dryness because hexavalent chromium may be lost due to reaction with the PVC filter and/or co-collected aerosol constituents. An indication that hexavalent chromium has been lost in this manner is a brown-colored PVC filter.

NOTE: A hot plate, heater block, or ultrasonic bath can also be used for this step [9, 11].

- a. Cool the solution and transfer it quantitatively with distilled water rinses to a 25-mL volumetric flask. Bring to volume with distilled water.

NOTE: If the solution is cloudy, filter an aliquot through a PTFE luer lock filter attached to a syringe.

- b. Transfer an aliquot of the solution to the appropriate vial for the chromatograph's autosampler and analyze (steps 9 through 13).

#### **CALIBRATION AND QUALITY CONTROL:**

6. Calibrate daily with at least six working standards. Transfer 5 mL of extraction solution to each of a series of 25-mL volumetric flasks. Pipet known volumes (0 to 5 mL) of calibration stock solution (1.0 µg/mL) into the volumetric flasks. For higher standards, pipet 10 - 20 µL of the 1000 µg/mL concentrated stock and bring the volume to 25 mL with distilled water. These working standards contain 0 to 20 µg Cr(VI) per sample.
7. Analyze the working standards together with blanks and samples (steps 9 through 13).
8. Prepare a calibration graph [instrument response vs. µg Cr(VI)].

#### **MEASUREMENT:**

9. Set wavelength on the detector to 540 nm.
10. Set the liquid chromatograph to manufacturer's recommendations and parameters given on page 7605-1. With a mobile phase flow rate of 1.0 mL/min., a post-column reagent flow rate of 0.7 mL/min., and a 2.2-m post-column tube, the derivative retention time should be approximately 3.7 - 4.7 minutes.  
NOTE: If the instrument response for the samples is higher than the standards, dilute using a 1:5 dilution of extraction solution:water to maintain a constant ionic strength; repeat the analysis; and multiply the measured concentration by the appropriate dilution factor. Alternatively, inject a smaller volume and multiply by the appropriate factor.
11. After the analysis is complete, flush the entire system with ASTM Type II water for at least one hour at 1.0 mL/min. with all columns on line. Remove the columns and continue flushing for an additional two hours. Flush the autosampler with several injections of water. Leaving the columns in line while the system is idle is not recommended.

**CALCULATIONS:**

12. From the calibration graph, determine the mass of Cr(VI) in each sample, W ( $\mu\text{g}$ ), and in the average blank, B ( $\mu\text{g}$ ).
13. Calculate concentration, C ( $\text{mg}/\text{m}^3$ ), of Cr(VI) in the air volume sampled, V (L):

$$C = \frac{W - B}{V}, \text{mg} / \text{m}^3$$

NOTE:  $\mu\text{g}/\text{L} = \text{mg}/\text{m}^3$

**EVALUATION OF METHOD:**

This method was evaluated in the laboratory with spiked filters and a certified reference material containing a known loading of Cr(VI). This certified reference material (CRM) is European Commission, Institute for Reference Materials and Measurements EC/IRMM) CRM 545, Cr(VI) and Cr(total) in welding dust loaded on a glass fiber filter [12]. This method was evaluated for extraction efficiency over the concentration range of 0.15 - 5  $\mu\text{g}/\text{sample}$  testing two brands of filters, SILICAL® and GLA-5000™[3]. In these experiments, test atmospheres were not generated; instead, Cr(VI) as the dichromate was fortified on the face of the sample filters, then 240 L of air with 35% relative humidity was pulled through at 1 L/min. A 30-day storage study using both types of filters was conducted at 1.5  $\mu\text{g}/\text{sample}$  (30x LOQ) at ambient room temperature and 4 °C. The average recovery of the stored samples was 94.8%. The estimation of the limit of detection and limit of quantitation (LOD/LOQ), were determined analyzing a series of liquid standards. The LOD and LOQ, 0.02  $\mu\text{g}/\text{sample}$  and 0.07  $\mu\text{g}/\text{sample}$  respectively were calculated by Burkart's method [13].

To fully evaluate this method, a field-study was conducted in which side-by-side samples were taken to measure exposures to Cr(VI) during spray-painting and electroplating operations. These samples were analyzed subsequently by 4 different methods (NIOSH Method 7605, 7703, 7300 and OSHA ID-215) [1]. NIOSH method 7300 was used to measure total chromium. The results from the other 3 methods correlated very well showing no statistical difference among the 3 methods. Recoveries of 98.4 ( $\pm$  3.4) % were obtained for CRM 545 (n = 6) [2].

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# Material Safety Data Sheet



ARCAL 25 - 75% Argon, 25% Carbon Dioxide

## 1. Product and company identification

**Product name** : ARCAL 25 - 75% Argon, 25% Carbon Dioxide  
**Material uses** : Not available.  
**Code** : 10094  
**Supplier/Manufacturer** : Air Liquide America Specialty Gases LLC  
2700 Post Oak Drive  
Houston, TX 77056-8229  
USA  
  
GENERAL MSDS INFORMATION: 1-713-896-2896  
**Validation date** : 11/02/2010.  
**Prepared by** : Atrion Regulatory Services, Inc.  
**In case of emergency** : CHEMTREC: 1(800) 424 – 9300

## 2. Hazards identification

**Physical state** : Gas.  
**Color** : Colorless.  
**Odor** : Odorless.  
**Emergency overview**  
**Signal word** : CAUTION!  
**Hazard statements** : HIGH PRESSURE GAS. GAS REDUCES OXYGEN AVAILABLE FOR BREATHING. CONTAINS MATERIAL THAT MAY CAUSE TARGET ORGAN DAMAGE, BASED ON ANIMAL DATA.  
  
**Precautions** : Contains gas under pressure. In a fire or if heated, a pressure increase will occur and the container may burst or explode. At very high concentrations, can displace the normal air and cause suffocation from lack of oxygen. Do not puncture or incinerate container. Do not enter storage areas and confined spaces unless adequately ventilated. Avoid breathing gas. Use only with adequate ventilation. Keep container tightly closed and sealed until ready for use.  
  
**OSHA/HCS status** : This material is considered hazardous by the OSHA Hazard Communication Standard (29 CFR 1910.1200).  
**Routes of entry** : Inhalation.  
**Potential acute health effects**  
**Inhalation** : At very high concentrations, can displace the normal air and cause suffocation from lack of oxygen.  
**Ingestion** : As this product is a gas, refer to the inhalation section.  
**Skin** : Contact with rapidly expanding gas may cause burns or frostbite.  
**Eyes** : Contact with rapidly expanding gas may cause burns or frostbite.  
**Potential chronic health effects**  
**Chronic effects** : Contains material that may cause target organ damage, based on animal data.  
**Carcinogenicity** : No known significant effects or critical hazards.  
**Mutagenicity** : No known significant effects or critical hazards.  
**Teratogenicity** : No known significant effects or critical hazards.  
**Developmental effects** : No known significant effects or critical hazards.

## 2. Hazards identification

- Fertility effects** : No known significant effects or critical hazards.
- Target organs** : Contains material which may cause damage to the following organs: lungs, cardiovascular system, skin, eyes, central nervous system (CNS).

### Over-exposure signs/symptoms

- Inhalation** : No specific data.
- Ingestion** : No specific data.
- Skin** : No specific data.
- Eyes** : No specific data.
- Medical conditions aggravated by over-exposure** : Pre-existing disorders involving any target organs mentioned in this MSDS as being at risk may be aggravated by over-exposure to this product.

## 3. Composition/information on ingredients

Name	CAS number	%
argon	7440-37-1	75
carbon dioxide	124-38-9	25

There are no additional ingredients present which, within the current knowledge of the supplier and in the concentrations applicable, are classified as hazardous to health or the environment and hence require reporting in this section.

## 4. First aid measures

- Eye contact** : Check for and remove any contact lenses. Immediately flush eyes with plenty of water for at least 15 minutes, occasionally lifting the upper and lower eyelids. Get medical attention immediately.
- Skin contact** : In case of contact, immediately flush skin with plenty of water for at least 15 minutes while removing contaminated clothing and shoes. Wash clothing before reuse. Clean shoes thoroughly before reuse. Get medical attention immediately.
- Inhalation** : Move exposed person to fresh air. If not breathing, if breathing is irregular or if respiratory arrest occurs, provide artificial respiration or oxygen by trained personnel. Loosen tight clothing such as a collar, tie, belt or waistband. Get medical attention immediately.
- Ingestion** : As this product is a gas, refer to the inhalation section.
- Protection of first-aiders** : No action shall be taken involving any personal risk or without suitable training. If it is suspected that fumes are still present, the rescuer should wear an appropriate mask or self-contained breathing apparatus. It may be dangerous to the person providing aid to give mouth-to-mouth resuscitation.
- Notes to physician** : No specific treatment. Treat symptomatically. Contact poison treatment specialist immediately if large quantities have been ingested or inhaled.

## 5. Fire-fighting measures

- Flammability of the product** : Non-flammable gas. Contains gas under pressure. In a fire or if heated, a pressure increase will occur and the container may burst or explode.

### Extinguishing media

- Suitable** : Use an extinguishing agent suitable for the surrounding fire.
- Not suitable** : None known.

## 5. Fire-fighting measures

- Special exposure hazards** : Promptly isolate the scene by removing all persons from the vicinity of the incident if there is a fire. No action shall be taken involving any personal risk or without suitable training. Contact supplier immediately for specialist advice. Move containers from fire area if this can be done without risk. Use water spray to keep fire-exposed containers cool.
- Hazardous thermal decomposition products** : Decomposition products may include the following materials:  
carbon dioxide  
carbon monoxide
- Special protective equipment for fire-fighters** : Fire-fighters should wear appropriate protective equipment and self-contained breathing apparatus (SCBA) with a full face-piece operated in positive pressure mode.

## 6. Accidental release measures

- Personal precautions** : No action shall be taken involving any personal risk or without suitable training. Evacuate surrounding areas. Keep unnecessary and unprotected personnel from entering. Avoid breathing gas. Provide adequate ventilation. Wear appropriate respirator when ventilation is inadequate. Put on appropriate personal protective equipment (see Section 8).
- Environmental precautions** : Ensure emergency procedures to deal with accidental gas releases are in place to avoid contamination of the environment.
- Methods for cleaning up**
- Small spill** : Immediately contact emergency personnel. Stop leak if without risk.
- Large spill** : Immediately contact emergency personnel. Stop leak if without risk. Note: see section 1 for emergency contact information and section 13 for waste disposal.

## 7. Handling and storage

- Handling** : Put on appropriate personal protective equipment (see Section 8). Eating, drinking and smoking should be prohibited in areas where this material is handled, stored and processed. Workers should wash hands and face before eating, drinking and smoking. Remove contaminated clothing and protective equipment before entering eating areas. Contains gas under pressure. Avoid contact with eyes, skin and clothing. Avoid breathing gas. Use only with adequate ventilation. Wear appropriate respirator when ventilation is inadequate. Empty containers retain product residue and can be hazardous. Do not puncture or incinerate container.
- Storage** : Store in accordance with local regulations. Store in a segregated and approved area. Store in a dry, cool and well-ventilated area, away from incompatible materials (see Section 10). Keep container tightly closed and sealed until ready for use.

## 8. Exposure controls/personal protection

### United States

Ingredient	Exposure limits
argon carbon dioxide	Oxygen Depletion [Asphyxiant] <b>ACGIH TLV (United States, 1/2009).</b> TWA: 5000 ppm 8 hour(s). TWA: 9000 mg/m <sup>3</sup> 8 hour(s). STEL: 30000 ppm 15 minute(s). STEL: 54000 mg/m <sup>3</sup> 15 minute(s). <b>OSHA PEL 1989 (United States, 3/1989).</b> TWA: 10000 ppm 8 hour(s). TWA: 18000 mg/m <sup>3</sup> 8 hour(s). STEL: 30000 ppm 15 minute(s).



## 8. Exposure controls/personal protection

STEL: 54000 mg/m<sup>3</sup> 15 minute(s).  
**NIOSH REL (United States, 6/2008).**  
 TWA: 5000 ppm 10 hour(s).  
 TWA: 9000 mg/m<sup>3</sup> 10 hour(s).  
 STEL: 30000 ppm 15 minute(s).  
 STEL: 54000 mg/m<sup>3</sup> 15 minute(s).  
**OSHA PEL (United States, 11/2006).**  
 TWA: 5000 ppm 8 hour(s).  
 TWA: 9000 mg/m<sup>3</sup> 8 hour(s).

- Recommended monitoring procedures** : If this product contains ingredients with exposure limits, personal, workplace atmosphere or biological monitoring may be required to determine the effectiveness of the ventilation or other control measures and/or the necessity to use respiratory protective equipment.
- Engineering measures** : Use only with adequate ventilation. Use process enclosures, local exhaust ventilation or other engineering controls to keep worker exposure to airborne contaminants below any recommended or statutory limits.
- Hygiene measures** : Wash hands, forearms and face thoroughly after handling chemical products, before eating, smoking and using the lavatory and at the end of the working period. Appropriate techniques should be used to remove potentially contaminated clothing. Wash contaminated clothing before reusing. Ensure that eyewash stations and safety showers are close to the workstation location.
- Personal protection**
- Respiratory** : Use a properly fitted, air-purifying or air-fed respirator complying with an approved standard if a risk assessment indicates this is necessary. If operating conditions cause high gas concentrations to be produced or any recommended or statutory exposure limit is exceeded, use an air-fed respirator or self-contained breathing apparatus. The gas can cause asphyxiation without warning by replacing the oxygen in the air. Respirator selection must be based on known or anticipated exposure levels, the hazards of the product and the safe working limits of the selected respirator.
- Hands** : Chemical-resistant, impervious gloves complying with an approved standard should be worn at all times when handling chemical products if a risk assessment indicates this is necessary.
- Eyes** : Safety eyewear complying with an approved standard should be used when a risk assessment indicates this is necessary to avoid exposure to liquid splashes, mists or dusts.
- Skin** : Personal protective equipment for the body should be selected based on the task being performed and the risks involved and should be approved by a specialist before handling this product.
- Environmental exposure controls** : Emissions from ventilation or work process equipment should be checked to ensure they comply with the requirements of environmental protection legislation. In some cases, fume scrubbers, filters or engineering modifications to the process equipment will be necessary to reduce emissions to acceptable levels.

## 9. Physical and chemical properties

- Physical state** : Gas.
- Color** : Colorless.
- Odor** : Odorless.
- Boiling/condensation point** : -185.7°C (-302.3°F)
- Melting/freezing point** : -189.2°C (-308.6°F)
- Critical temperature** : -122.4°C (-188.3°F)

## 9. Physical and chemical properties

<b>Density</b>	: 1.65 g/cm <sup>3</sup>
<b>Vapor density</b>	: 1.38 [Air = 1]
<b>Viscosity</b>	: Not available.

## 10. Stability and reactivity

<b>Chemical stability</b>	: The product is stable.
<b>Conditions to avoid</b>	: Avoid excessive heat.
<b>Incompatible materials</b>	: Not available.
<b>Hazardous decomposition products</b>	: Under normal conditions of storage and use, hazardous decomposition products should not be produced.
<b>Possibility of hazardous reactions</b>	: Under normal conditions of storage and use, hazardous reactions will not occur.  Under normal conditions of storage and use, hazardous polymerization will not occur.

## 11. Toxicological information

### Acute toxicity

Not available.

### Chronic toxicity

Not available.

### Irritation/Corrosion

Not available.

### Sensitizer

Not available.

### Carcinogenicity

#### Classification

Not available.

### Mutagenicity

Not available.

### Teratogenicity

Not available.

### Reproductive toxicity

Not available.

## 12. Ecological information

**Ecotoxicity** : No known significant effects or critical hazards.

### Aquatic ecotoxicity

Not available.

### Persistence/degradability

Not available.




### 13. Disposal considerations

**Waste disposal** : The generation of waste should be avoided or minimized wherever possible. Empty containers or liners may retain some product residues. This material and its container must be disposed of in a safe way. Dispose of surplus and non-recyclable products via a licensed waste disposal contractor. Disposal of this product, solutions and any by-products should at all times comply with the requirements of environmental protection and waste disposal legislation and any regional local authority requirements. Do not puncture or incinerate container. Empty pressure vessels should be returned to the supplier.

Disposal should be in accordance with applicable regional, national and local laws and regulations.

Refer to Section 7: HANDLING AND STORAGE and Section 8: EXPOSURE CONTROLS/PERSONAL PROTECTION for additional handling information and protection of employees.

### 14. Transport information

Regulatory information	UN number	Proper shipping name	Classes	PG*	Label	Additional information
<b>DOT Classification</b>	UN1956	Compressed gas, n.o.s. (Argon)	2.2	-		<p><b>Limited quantity</b> Yes.</p> <p><b>Packaging instruction</b> <b>Passenger aircraft</b> Quantity limitation: 75 kg</p> <p><b>Cargo aircraft</b> Quantity limitation: 150 kg</p> <p><b>Special provisions</b> 77</p>
<b>IMDG Class</b>	UN1956	COMPRESSED GAS, N.O.S. (Argon)	2.2	-		<p><b>Emergency schedules (EmS)</b> F-C, S-V</p>
<b>IATA-DGR Class</b>	UN1956	Compressed gas, n.o.s. (Argon)	2.2	-		<p><b>Passenger and Cargo Aircraft</b>Quantity limitation: 75 kg Packaging instructions: 200</p> <p><b>Cargo Aircraft Only</b>Quantity limitation: 150 kg Packaging instructions: 200</p> <p><b>Limited Quantities - Passenger Aircraft</b>Quantity limitation: Forbidden Packaging instructions: Forbidden</p>

PG\* : Packing group

### 15. Regulatory information

**HCS Classification** : Compressed gas  
Target organ effects

**U.S. Federal regulations** : **TSCA 8(a) IUR**: Partial exemption  
**United States inventory (TSCA 8b)**: All components are listed or exempted.

## 15. Regulatory information

**SARA 302/304/311/312 extremely hazardous substances:** No products were found.  
**SARA 302/304 emergency planning and notification:** No products were found.  
**SARA 302/304/311/312 hazardous chemicals:** Argon; carbon dioxide  
**SARA 311/312 MSDS distribution - chemical inventory - hazard identification:**  
 Argon: Sudden release of pressure; carbon dioxide : Sudden release of pressure,  
 Immediate (acute) health hazard, Delayed (chronic) health hazard

**Clean Air Act (CAA) 112 accidental release prevention:** No products were found.

**Clean Air Act Section 112(b) Hazardous Air Pollutants (HAPs)** : Not listed

**Clean Air Act Section 602 Class I Substances** : Not listed

**Clean Air Act Section 602 Class II Substances** : Not listed

**DEA List I Chemicals (Precursor Chemicals)** : Not listed

**DEA List II Chemicals (Essential Chemicals)** : Not listed

### SARA 313

**Form R - Reporting requirements** : Not applicable.

**Supplier notification** : Not applicable.

### State regulations

**Massachusetts** : The following components are listed: ARGON; CARBON DIOXIDE

**New York** : None of the components are listed.

**New Jersey** : The following components are listed: ARGON; CARBON DIOXIDE

**Pennsylvania** : The following components are listed: ARGON; CARBON DIOXIDE

**Canada inventory** : All components are listed or exempted.

### International regulations

**International lists** : **Australia inventory (AICS):** All components are listed or exempted.  
**China inventory (IECSC):** All components are listed or exempted.  
**Japan inventory:** Not determined.  
**Korea inventory:** All components are listed or exempted.  
**New Zealand Inventory of Chemicals (NZIoC):** All components are listed or exempted.  
**Philippines inventory (PICCS):** All components are listed or exempted.

**Chemical Weapons Convention List Schedule I Chemicals** : Not listed

**Chemical Weapons Convention List Schedule II Chemicals** : Not listed

**Chemical Weapons Convention List Schedule III Chemicals** : Not listed

## 16. Other information

**Label requirements** : HIGH PRESSURE GAS. GAS REDUCES OXYGEN AVAILABLE FOR BREATHING. CONTAINS MATERIAL THAT MAY CAUSE TARGET ORGAN DAMAGE, BASED ON ANIMAL DATA.

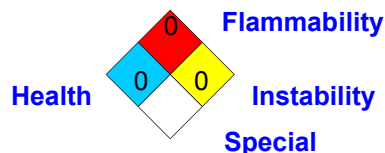
**Hazardous Material Information System (U.S.A.)** :

Health	*	0
Flammability		0
Physical hazards		2

Caution: HMIS® ratings are based on a 0-4 rating scale, with 0 representing minimal hazards or risks, and 4 representing significant hazards or risks. Although HMIS® ratings are not required on MSDSs under 29 CFR 1910.1200, the preparer may choose to provide them. HMIS® ratings are to be used with a fully implemented HMIS® program. HMIS® is a registered mark of the National Paint & Coatings Association (NPCA). HMIS® materials may be purchased exclusively from J. J. Keller (800) 327-6868.

The customer is responsible for determining the PPE code for this material.

**National Fire Protection Association (U.S.A.)** :



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Copyright ©2001, National Fire Protection Association, Quincy, MA 02269. This warning system is intended to be interpreted and applied only by properly trained individuals to identify fire, health and reactivity hazards of chemicals. The user is referred to certain limited number of chemicals with recommended classifications in NFPA 49 and NFPA 325, which would be used as a guideline only. Whether the chemicals are classified by NFPA or not, anyone using the 704 systems to classify chemicals does so at their own risk.

**Date of issue** : 11/02/2010.

**Date of previous issue** : No previous validation.

**Version** : 1

☑ Indicates information that has changed from previously issued version.

### Notice to reader

This Material Safety Data Sheet is offered pursuant to OSHA's Hazard Communication Standard, 29 CFR, 1910.1200, American National Standard Institute Z400.1, 2004. Other government regulations must be reviewed for applicability to this gas mixture. To the best of Air Liquide's knowledge, the information contained herein is reliable and accurate as of this date; however, accuracy, suitability or completeness are not guaranteed and no warranties of any type, either express or implied, are provided. The information contained herein relates only to this specific product. If this gas mixture is combined with other materials, all component properties must be considered. Data may be changed from time to time. Be sure to consult the latest edition.