

HEXAVALENT CHROMIUM



Method number: W4001

Target concentration: 0.050 $\mu\text{g}/100 \text{ cm}^2$

Procedure: Wipe samples are collected by using firm hand pressure to move a 37-mm diameter polyvinyl chloride (PVC) filter, 5- μm pore size, across the surface of interest. An alternate medium for rough surfaces is a 37-mm binderless quartz fiber filter. Samples are digested with multiple buffered solutions. After dilution, an aliquot of this solution is analyzed for hexavalent chromium (Cr(VI)) by ion chromatography with postcolumn derivatization of the Cr(VI) with 1,5-diphenyl carbazide and detected by a UV-vis detector at 540 nm.

Special requirements: In chrome plating environments, wipe samples taken on a PVC filter or an uncoated binderless quartz fiber filter, should be placed in a vial containing 5 mL of an aqueous solution containing 10% Na_2CO_3 with 2% NaHCO_3 immediately after sampling to eliminate the interference from the acid used in the chrome plating process. An alternate medium which does not require extraction in the field is a binderless quartz fiber filter coated with 1% NaOH.

Reliable quantitation limit: 3 ng/sample

Status of method: Evaluated method. This method has been subjected to the established evaluation procedures of the Methods Development Team.

April 2001

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1. General Discussion

1.1 Background

1.1.1 History

This wipe sampling method was developed to provide a means of taking wipe samples for hexavalent chromium (Cr(VI)). The OSHA SLTC has received wipe samples taken on a variety of media, including PVC filters, baby wipes, paper filters such as Whatman filter, glass fiber filter, and mixed cellulose ester filter. The Cr(VI) decomposed to trivalent chromium (Cr(III)) on all of these media except the PVC filters. The Evaluation Guidelines for Surface Sampling Methods¹ specifies the use of fabric wipes, whenever possible. The cloth-like wipes which were tried, Durx 670 (polyester/cotton nonwoven fabric) and pro-Wipe 880 (polyester woven fabric), did not work because the Cr(VI) reacted with them, changing it to Cr(III), so they could not be used for this evaluation. Wipe samples were first evaluated by collection on PVC filters, and analyzed following the analytical procedure in OSHA Method ID-215.² Because PVC filters may tear on rough surfaces, a binderless quartz fiber filter was also evaluated and found to have good recoveries. In chrome plating processes, there is an additional interference of the acid, which changes the Cr(VI) to Cr(III), upon storage. Both the samples collected on the PVC filters and the binderless quartz fiber filters had a significant loss in a 15 day storage. This loss was eliminated by placing the samples taken on either the PVC filters or the binderless quartz fiber filters in a vial containing 5-mL of an aqueous solution containing 10% sodium carbonate (Na₂CO₃)/2% sodium bicarbonate (NaHCO₃) immediately after sampling. An alternate medium, which requires no field extraction, binderless quartz fiber filters coated with 1% NaOH, was also evaluated for sampling in the chrome plating environment, and found to give good recoveries.

A glass plate was first chosen for an ideal surface to check the surface sampler removal efficiency, but Cr(VI) interacted with the glass plate changing to Cr(III). The PTFE surface was chosen as an ideal surface for this method because of its inertness, and it gave good recoveries for wipe sampling.

Following the procedure in OSHA Method ID-215³, the filters, of all types, had extraction and digestion with multiple buffers, separation by ion chromatography, with post-column derivatization and detection by UV-vis at 540 nm. In this evaluation, the filter is digested in an aqueous solution containing 10% sodium carbonate (Na₂CO₃)/2% sodium bicarbonate (NaHCO₃) and the mixture of phosphate buffer/magnesium sulfate. After dilution with DI water, an aliquot of this solution is analyzed for Cr(VI) using an ion chromatograph equipped with a UV-vis detector at 540 nm. A post-column derivatization of the Cr(VI) with 1,5-diphenyl carbazide is performed prior to detection. The phosphate buffer and magnesium sulfate solutions are added to precipitate other metals, especially Fe(II), so that they do not reduce Cr(VI) changing it to Cr(III). This was shown in the interferences studies in OSHA Method ID-215⁴. The Cr(III) is also precipitated to prevent it from oxidizing to Cr(VI).

For analysis of samples taken in spray paint operations, it is necessary to perform a second extraction of the filter with an aqueous solution of 5% NaOH/ 7.5% Na₂CO₃, with the addition of the phosphate buffer/magnesium sulfate, to remove the Cr(VI) from the

¹ Lawrence, R. *Evaluation Guidelines for Surface Sampling Methods*; OSHA Salt Lake Technical Center, U.S. Department of Labor: Salt Lake City, UT, 2001, unpublished.

² Ku, J., Eide, M., ID-215 Hexavalent Chromium, 1998, <http://www.osha.gov>, (accessed May 2000)

³ Ku, J., Eide, M., ID-215 Hexavalent Chromium, 1998, <http://www.osha.gov>, (accessed May 2000)

⁴ Ku, J., Eide, M., ID-215 Hexavalent Chromium, 1998, <http://www.osha.gov>, (accessed May 2000)

hardened paint matrix. Again, the phosphate buffer with the magnesium sulfate is added to the NaOH/Na₂CO₃ to precipitate the other metals, and prevent them from interacting with the Cr(VI).

Samples taken in a chrome plating operation have the additional interference of the acid or acids, which convert the Cr(VI) to Cr(III), as the samples are stored. The chrome plating bath usually contains sulfuric acid, so a mixture of sulfuric acid and Cr(VI) in water was prepared to emulate the chrome plating solution. The recovery on Day 15 of storage at ambient temperature was 78.0% for PVC filters spiked with this mixture of Cr(VI) and H₂SO₄, and 81.0% for refrigerated samples. Samples taken of this mixture of Cr(VI) and H₂SO₄ on PVC filters, immediately placed into a vial containing a solution of 10% Na₂CO₃ with 2% NaHCO₃ after sampling, to neutralize the acid, and stored at ambient temperature had a 97.4% recovery on Day 15. Binderless quartz fiber filters had a loss of Cr(VI) when stored, with an ambient recovery of 86.1% on Day 15. When the binderless quartz fiber filters were placed immediately into a vial containing a solution of 10% Na₂CO₃ with 2% NaHCO₃ after sampling, the ambient recovery was 97.9% on Day 15. The method for collecting Cr(VI) air samples in chrome plating operations used in the UK is with a binderless quartz fiber filter coated with 1% NaOH.⁵ The NaOH coating neutralizes the acid or acids, halting their reaction with the Cr(VI). The recovery of Cr(VI) from wipe samples spiked with the mixture of Cr(VI) and H₂SO₄ using the 1% NaOH coated binderless quartz fiber filters had a recovery of 96.4% for ambient samples on Day 15. The 1% NaOH coated binderless quartz fiber filters are digested and analyzed in the same fashion as the PVC filters. These storage results indicate that for samples taken in chrome plating operations, the uncoated filters should be placed into a vial containing a solution of 10% Na₂CO₃ with 2% NaHCO₃ after sampling, or a 1% NaOH coated binderless quartz fiber filter should be used.

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

Some of the water soluble salts of chromic acid, (potassium dichromate, potassium chromate, sodium dichromate, and sodium chromate) are very corrosive and can cause burns which can facilitate the adsorption of these compounds through the skin.⁶ Cr(VI) causes skin ulcers, blisters, burns, irritation to mucous membranes, and eye irritation. Workers sensitized to Cr(VI) compounds experience allergic dermatitis reactions. Acute dermal exposure can result in necrosis of the skin and underlying tissue and sloughing of the skin.⁷ Kidney damage has been reported in workers where skin absorption has occurred. There have been reports of lung cancer in workers exposed to chrome pigments in Germany, Norway, and the United States.⁸ ACGIH has a TLV of 0.05 mg/m³ for water soluble Cr(VI) compounds and 0.01 mg/m³ for insoluble Cr(VI) compounds and classify them as recognized human carcinogens.⁹

⁵ Foster, R., Usher, J, and Howe, A. Hexavalent Chromium in Chromium Plating Mists, 1998, MDHS method 52/3, Health and Safety Executive, Sheffield UK.

⁶ *Toxicological Profile for Chromium (update)*, draft for public comment, U.S. Department of Health and Human Services, Public Health Service, Agency for Toxic Substances and Disease Registry, 1998, p 97.

⁷ *Toxicological Profile for Chromium (update)*, draft for public comment, U.S. Department of Health and Human Services, Public Health Service, Agency for Toxic Substances and Disease Registry, 1998, p 105.

⁸ *Documentation of the Threshold Limit Values and Biological Exposure Indices*, 6th ed.; American Conference of Governmental Industrial Hygienists, Inc.: Cincinnati, OH, 1991, Vol. II, p.313.

⁹ *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.

ACGIH recommends BEI (Biological Exposure Indices) not exceed 10 µg/g creatinine for the increase in urinary chromium concentrations during the workshift, obtained by comparing a urine sample from before the shift to one at the end of the shift, and 30 µg/g creatinine for the end of the workweek at the end of the shift. The chromium measured in urine is Cr(III), as Cr(VI) is enzymatically reduced to Cr(III). The preshift urine sample is necessary because Cr(III) is a nutrient necessary for humans, and it is often included in vitamin preparations, or is taken as a supplement. Other common sources of chromium are smoking and water supplies. The BEI is based on the difference between the two urine samples.¹⁰

1.1.3 Workplace exposure¹¹

Cr(VI) is primarily used in the form of chromium trioxide, and the chromates and dichromates of sodium, potassium, ammonium, calcium, barium, zinc, strontium, and lead. These compounds are used in photography, dyeing, electroplating, paints, as rust inhibitors, as pigments, and as oxidizing agents in tanning.

1.1.4 Physical properties¹² (the physical properties listed below are for chromium trioxide, for physical properties of the other common salts containing Cr(VI) see OSHA Method ID-215¹³)

synonyms:	chromic acid, chromic anhydride, chromia, chromic trioxide		
CAS number:	1333-82-0	IMIS number:	0686 ¹⁴
molecular weight:	100.01	melting point:	196 °C
structural formula:	CrO ₃	solubility:	very sol in water, insol in alcohol
appearance:	dark purple-red crystals		
fire and explosion hazard:	a very powerful oxidizing agent, which can cause violent reactions when in contact with organic matter or reducing agents		

This method was evaluated according to the OSHA SLTC "Evaluation Guidelines for Surface Sampling Methods".¹⁵ The Guidelines define analytical parameters, specify required laboratory tests, statistical calculations and acceptance criteria. The analyte surface concentrations throughout this method are based on the recommended sampling and analytical parameters.

1.2 Limit defining parameters

1.2.1 Detection limit of the analytical procedure

The DLAP was calculated to be 0.09 ng. This is the lowest amount of analyte that will give a detector response that is significantly different from the response of a reagent blank. (Section 4.1)

¹⁰ *Documentation of the Threshold Limit Values and Biological Exposure Indices*, 6th ed.; American Conference of Governmental Industrial Hygienists, Inc.: Cincinnati, OH, 1991, Vol. III, p BEI-69.

¹¹ *Documentation of the Threshold Limits Value and Biological Exposure Indices*, 6th ed., American Conference of Governmental Industrial Hygienists, Inc., Cincinnati OH, 1991 Vol. 1, pp 312-315.

¹² Budavari, S., *The Merck Index*, 12th ed., Merck & Co. Inc.: Whitehouse Station, NJ, 1996, p 375.

¹³ Ku, J., Eide, M., ID-215 Hexavalent Chromium, 1998, <http://www.osha.gov>, (accessed May 2000)

¹⁴ OSHA Computerized Information System Database, Chemical Sampling Information, <http://www.osha.gov>, (accessed May 2000)

¹⁵ Lawrence, R. *Evaluation Guidelines for Surface Sampling Methods*; OSHA Salt Lake Technical Center, U.S. Department of Labor: Salt Lake City, UT, 2001, unpublished.

1.2.2 Detection limit of the overall procedure

The detection limit of the overall procedure for PVC filters is 0.91 ng per sample, binderless quartz fiber filters is 0.67 ng per sample, and 1% NaOH coated binderless quartz fiber filters is 0.94 ng per sample. This is the lowest amount of Cr(VI) spiked on the wipe sampler that will give a detector response that is significantly different from the response of wipe sampler blanks. (Section 4.2)

1.2.3 Reliable quantitation limit

The reliable quantitation limit for PVC filters is 3.04 ng per sample, binderless quartz fiber filters is 2.23 ng per sample, and 1% NaOH coated binderless quartz fiber filters is 3.12 ng per sample. This is the lowest amount of Cr(VI) spiked on the wipe sampler that will give a detector response that is considered the lower limit for precise quantitative measurements. (Section 4.2)

1.2.4 Recovery

The recovery of Cr(VI) from samples spiked on PVC filters used in a 15-day storage test remained above 96.4% when the samples were stored at 22 °C. (Section 4.3)

The recovery of Cr(VI) from samples spiked on binderless quartz fiber filters used in a 15-day storage test remained above 96.4 % when the samples were stored at 22 °C. (Section 4.3)

The recovery of Cr(VI) from samples spiked with a mixture of H₂SO₄ and Cr(VI)(to simulate a chrome plating operation) on PVC filters, then immediately placed into a vial containing 5 mL of an aqueous solution containing 10% Na₂CO₃ with 2% NaHCO₃, used in a 15-day storage test, remained above 97.9% when the samples were stored at 22 °C. (Section 4.3)

The recovery of Cr(VI) from samples spiked with a mixture of H₂SO₄ and Cr(VI)(to simulate a chrome plating operation) on binderless quartz fiber filters, then immediately placed into a vial containing 5 mL of an aqueous solution containing 10% Na₂CO₃ with 2% NaHCO₃, used in a 15-day storage test, remained above 97.9% when the samples were stored at 22 °C. (Section 4.3)

The recovery of Cr(VI) from samples spiked with a mixture of H₂SO₄ and Cr(VI)(to simulate a chrome plating operation) on 1% NaOH coated binderless quartz fiber filters used in a 15-day storage test remained above 96.4% when the samples were stored at 22 °C. (Section 4.3)

1.2.5 Surface sampler removal efficiency

The removal efficiency of filters spiked with Cr(VI) at the target concentration of 0.05 µg/100 cm² is 96.8% for PVC, 97.7% for binderless quartz fiber filters, and 97.0% for binderless quartz fiber filters coated with 1% NaOH . This is the percentage of Cr(VI) that was removed from a sheet of PTFE that was spiked at the target concentration. (Section 4.4)

1.2.6 Sampling reproducibility and analytical reproducibility

Six PTFE surfaces were spiked at the target concentration. A chemist, other than the one developing the method, conducted sampling on the PTFE surfaces, with the filters, as described in Section 2. The test was repeated with a second chemist performing the sampling. The samples were analyzed. For the PVC filters the first chemist was able to achieve a removal efficiency of 96.0%, and the second chemist was able to achieve a removal efficiency of 95.1%. (Section 4.6.1) For the binderless quartz fiber filters the first chemist was able to achieve a removal efficiency of 95.9%, and the second chemist was

able to achieve a removal efficiency of 96.0%. (Section 4.6.3) For the 1% NaOH coated binderless quartz fiber filters the first chemist was able to achieve a removal efficiency of 96.0%, and the second chemist was able to achieve a removal efficiency of 96.5%. (Section 4.6.5)

Six samples spiked on each of the three kinds of filters at the target concentration by liquid injection were submitted for analysis by the OSHA Salt Lake Technical Center. The samples on PVC filters were analyzed according to a draft copy of this procedure after 13 days of storage at 23 °C, with an average analytical result of 97.6% of theoretical (Section 4.6.2). The binderless quartz fiber filters were analyzed after 5 days of storage at 23 °C and had an average analytical result was 96.5% of theoretical (Section 4.6.4). The 1% NaOH coated binderless quartz fiber filters were analyzed after 9 days of storage at 23 °C, with an average analytical result was 95.8% of theoretical (Section 4.6.6).

2. Sampling Procedure

All safety practices that apply to the work area being sampled should be followed. Sampling should be conducted in such a manner that it will not interfere with work performance or safety. It is important to wear gloves when handling the 1% NaOH coated binderless quartz fiber filters as the NaOH coating is very caustic.

2.1 Apparatus

Samples are collected with 37-mm diameter polyvinyl chloride (PVC) filters 5- μ m pore size (MSA part # 625413).

On rough surfaces, samples are collected with 37-mm diameter binderless quartz fiber filters 0.45-mm thick (SKC part # 225-1809).

In chrome plating operations only, samples can be collected with 37-mm diameter 1% NaOH coated binderless quartz fiber filters 0.45-mm thick. (Section 4.9)

The selected gloves are to be resistant to penetration of the chemical being sampled and any other chemicals expected to be present. One pair of gloves per sample taken should be used to avoid cross contamination of samples.

Labeled vials, 20-mL glass scintillation vials or other appropriate sized glass vial with PTFE lined caps, one for each sample.

For samples taken in a chrome plating operation, 5 mL of an aqueous solution containing 10% Na_2CO_3 with 2% NaHCO_3 should be preloaded in the vials, if PVC or uncoated binderless quartz fiber filters are used for sampling.

2.2 Reagents

For samples taken in a chrome plating operation, 5 mL of an aqueous solution containing 10% Na_2CO_3 with 2% NaHCO_3 should be preloaded in the vials. (Section 3.2.15)

2.3 Technique

Prepare a sufficient number of vials, each labeled with a unique number, for the projected sampling needs.

Prepare a diagram of the area or rooms to be wipe sampled along with the locations of key surfaces.

Wear a new pair of clean gloves for each sample to prevent contamination of future samples as well as oneself. The selected gloves are to be resistant to penetration of the chemical being sampled

and any other chemicals expected to be present. PVC gloves are suggested for sampling Cr(VI) based on a review of a glove manufacturer's chemical resistivity and degradation information. Do not wear powdered gloves.

Record the sample vial number and the location where the sample is taken.

Remove the filter from the carrying container with clean PTFE-coated tweezers or plastic tweezers. Do not use metal tweezers to handle the filters as they will deposit Cr(VI) onto filters.

Depending on the purpose of the sample, it may be useful to determine the surface loading of the contamination (e.g., in micrograms of analyte per area). For these samples, it is necessary to record the area of the surface wiped (e.g., 100 cm²). This would not be necessary for samples taken to simply show the presence of the contaminant.

Surfaces should not be wetted with water as the water will allow any metal interferences to interact with the Cr(VI), thereby affecting the results.

Firm pressure should be applied when wiping. Start at the outside edge and progress toward the center making concentric squares of decreasing size. Fold the filter with the contaminant side inward and repeat.

Without allowing the filter to come into contact with any other surface, fold the filter with the exposed side inward. Place the filter in a sample vial, cap and place a corresponding number at the sample location on the diagram. Include notes with the sketch giving any further description that may prove useful when evaluating the sample results (e.g., a description of the surface sampled, such as : pencil, doorknob, safety glasses, lunch table, inside respirator, employee names, etc.).

PVC and binderless quartz fiber filter samples taken in a chrome plating operation should be placed in a vial containing 5 mL of an aqueous solution containing 10% Na₂CO₃ with 2% NaHCO₃ to stabilize the Cr(VI) to field extract them. An alternate media only for chrome plating operations is a binderless quartz fiber filter coated with 1% NaOH. The 1% NaOH coated binderless quartz fiber filters do not require field extraction. Gloves must be worn when handling these NaOH coated filters as the NaOH is very caustic.

Submit at least one blank wipe filter, treated in the same fashion, but without wiping.

Record sample location, employees names, surface area (if pertinent), work description, type of operation, personal protective equipment, and any other necessary information, along with any potential interferences on the OSHA-91A form.

Submit the samples to the OSHA Salt Lake Technical Center together with OSHA-91A forms as soon as possible after sampling. Ship any bulk samples separate from the surface samples.

2.4 Extraction efficiency

It is the responsibility of each analytical laboratory to determine the extraction efficiency because the wipe sampling media, reagents, and laboratory techniques may be different than those listed in this evaluation and could influence the results (Section 4.5).

The mean extraction efficiency for Cr(VI) from PVC filters over the range of 0.06 to 10 times the target concentration (3 to 500 nanograms per sample) was 96.6% for samples extracted with the first extraction buffer (10% Na₂CO₃ with 2% NaHCO₃) and 96.9% for samples extracted with the second extraction buffer (5% NaOH with 7.5% Na₂CO₃), used for spray paint samples only.

The mean extraction efficiency for Cr(VI) from binderless quartz fiber filters over the range of 0.06 to 10 times the target concentration (3 to 500 nanograms per sample) was 97.3% for samples extracted with the first extraction buffer (10% Na₂CO₃ with 2% NaHCO₃) and 96.2% for samples

extracted with the second extraction buffer (5% NaOH with 7.5% Na₂CO₃), used for spray paint samples only.

The mean extraction efficiency for Cr(VI) from 1% NaOH coated binderless quartz fiber filters over the range of 0.06 to 10 times the target concentration (3 to 500 nanograms per sample) was 97.3% for samples extracted with the first extraction buffer (10% Na₂CO₃ with 2% NaHCO₃) and 96.9% for samples extracted with the second extraction buffer (5% NaOH with 7.5% Na₂CO₃), used for spray paint samples only.

2.5 Interferences, sampling

Suspected interferences should be reported to the laboratory with submitted samples. The interference studies were performed in OSHA Method ID-215 Cr(VI)¹⁶. Cr(III) is the major positive interference and Fe(II) is the major negative interference. In chrome plating operations, the acid is also a negative interference.

3. Analytical Procedure

Adhere to the rules set down in your Chemical Hygiene Plan¹⁷. Avoid skin contact and inhalation of all chemicals and review all appropriate MSDSs before beginning the analysis of samples.

Analyze the samples using the analytical procedure in OSHA Method ID-215 Hexavalent Chromium.¹⁸

3.1 Apparatus

- 3.1.1 Ion chromatograph with a UV-vis detector and a postcolumn pump. A Dionex 4500i ion chromatograph with a UV-vis detector, a pneumatic controlled postcolumn reagent delivery system, and a reaction coil were used in this evaluation.
- 3.1.2 IC column and guard column which can separate Cr(VI) from any potential interferences. A 250-mm × 4-mm i.d. Dionex IonPac AS7 column and 50-mm × 4-mm i.d. Dionex IonPac NG1 guard column were used in this evaluation.
- 3.1.3 A means to integrate the chromatograms. The Dionex AI450 software, and a Millennium³² data system were used in this evaluation.
- 3.1.4 Automatic sampler. A Dionex model ASM-2, and sample vials, 0.5-mL, with filter caps was used in this evaluation.
- 3.1.5 Volumetric flasks, pipets, and calibrated micropipets.
- 3.1.6 Erlenmeyer flasks, 50-mL, for sample digestion.
- 3.1.7 Micro-analytical balance capable of weighing at least 0.01 mg.
- 3.1.8 Polyethylene bottles, 1-L size or larger, for extraction solutions.
- 3.1.9 Scintillation vials, glass, 20-mL.

¹⁶ Ku, J., Eide, M., ID-215 Hexavalent Chromium, 1998, <http://www.osha.gov>, (accessed May 2000)

¹⁷ Occupational Exposure to Chemicals in Laboratories. Code of Federal Regulations, Part 1910.1450, Title 29, 1998; www.osha.gov, standards, 5/12/2000.

¹⁸ Ku, J., Eide, M., ID-215 Hexavalent Chromium, 1998, <http://www.osha.gov>, (accessed May 2000)

- 3.1.10 Hotplate temperature adjustable to 135 °C placed in an exhaust hood.
- 3.1.11 Equipment for eluent degassing. A vacuum pump and ultrasonic bath were used for this evaluation.
- 3.1.12 Optional: Centrifuge for spinning down the precipitate in samples.

3.2 Reagents

- 3.2.1 Deionized water 18 MΩ. A Millipore Milli-Q system was used to prepare the water for this evaluation.
- 3.2.2 Sodium carbonate (NaCO_3), reagent grade. Mallinckrodt 99+% lot 7527 KHKC was used in this evaluation.
- 3.2.3 Sodium bicarbonate (NaHCO_3), reagent grade. Baker Analyzed Reagent 99.9% pure lot D12721 was used in this evaluation.
- 3.2.4 Potassium dichromate ($\text{K}_2\text{Cr}_2\text{O}_7$), reagent grade. JT Baker Reagent grade 99% lot 715426 and Acros lot A010583303 were used in this evaluation.
- 3.2.5 Magnesium sulfate (MgSO_4), anhydrous, reagent grade. ChemPure Reagent grade 99% lot M172KDHM was used in this evaluation.
- 3.2.6 Ammonium sulfate [$(\text{NH}_4)_2\text{SO}_4$], reagent grade. Aldrich 99+% lot OO427TQ was used in this evaluation.
- 3.2.7 Ammonium hydroxide (NH_4OH) 29% solution. Baker analyzed Reagent 28.9% NH_4OH lot 611248 was used in this evaluation.
- 3.2.8 1,5-Diphenylcarbazide (DPC) ($\text{C}_6\text{H}_5\text{NHNHCONHNHC}_6\text{H}_5$), reagent grade. Aldrich 99+% lot 03017AR was used in this evaluation.
- 3.2.9 Methyl alcohol (CH_3OH), HPLC grade. Fisher Optima 99.9% lot 966306 was used in this evaluation.
- 3.2.10 Sulfuric acid (H_2SO_4), concentrated. JT Baker Instra-analyzed 96.8% lot E24049 was used in this evaluation.
- 3.2.11 Nitric acid (HNO_3), concentrated (69-70%). JT Baker Instra-analyzed 69.0-70.0% lot N46048 was used in this evaluation.
- 3.2.12 Potassium hydrogenphosphate trihydrate ($\text{K}_2\text{HPO}_4 \cdot 3\text{H}_2\text{O}$), reagent grade. Aldrich 99+% lot 01525MN was used in this evaluation.
- 3.2.13 Potassium dihydrogenphosphate (KH_2PO_4), reagent grade. Aldrich 99+% lot 06327KQ was used in this evaluation.
- 3.2.14 Nitric acid solution (10%): In a 1-L flask place about 500-mL deionized water, add 100 mL concentrated nitric acid, then fill up to the mark with deionized water.
- 3.2.15 Buffer/extraction (BE) solution (2% NaHCO_3 with 10% Na_2CO_3): In a 1-L flask place about 500-mL deionized water, add 20 g of NaHCO_3 , swirl to dissolve, then add 100 g of Na_2CO_3 , and bring up to the mark with deionized water. Shake to dissolve or use an ultrasonic bath. Store in a polyethylene bottle.
- 3.2.16 Spray-paint extraction (SPE) solution (5% NaOH with 7.5% Na_2CO_3): In a 1-L flask place about 500-mL deionized water, add 50 g of NaOH , swirl to dissolve, then add 75 g of

Na_2CO_3 , and bring up to the mark with deionized water. Prepare the solution monthly, and store in a polyethylene bottle.

- 3.2.17 Magnesium sulfate solution: In a 100-mL volumetric flask place about 50 mL deionized water, add 9.9 g of anhydrous magnesium sulfate, mix well, and bring up to the mark with deionized water.
- 3.2.18 Phosphate buffer solution (0.5 M KH_2PO_4 with 0.5 M $\text{K}_2\text{HPO}_4 \cdot 3\text{H}_2\text{O}$): In a 1-L flask place about 500-mL deionized water, add 68 g of KH_2PO_4 and 114 g of $\text{K}_2\text{HPO}_4 \cdot 3\text{H}_2\text{O}$, swirl to dissolve and bring up to the mark with deionized water.
- 3.2.19 Phosphate buffer/Mg(II) (PBM) solution: In a 100-mL beaker place 50 mL of phosphate buffer, then add 25 mL of magnesium sulfate solution, and mix well. Prepare fresh before each analysis, as this solution is only good for 4 hours.
- 3.2.20 Dilute Buffer Extraction/Phosphate buffer/Mg(II) solution (DBE/PBM solution): In a 100-mL volumetric flask pipette 50 mL of BE solution, add 15 mL of PBM solution, bring up to the mark with deionized water, and mix. A precipitate of magnesium hydroxide will form and slowly precipitate out of solution. Allow the precipitation to settle for at least 60 minutes, or place in a 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.
- 3.2.21 Eluent [250 mM $(\text{NH}_4)_2\text{SO}_4$ with 100 mM NH_4OH]: In a 1-L flask place about 500 mL of deionized water, add 6.5 mL of the 29% ammonium hydroxide, then add 33 g of ammonium sulfate and mix well. Dilute up to the mark with deionized water. Degas the eluent before use. In this evaluation, the eluent was degassed with vacuum while in a ultrasonic bath. Transfer solution to the eluent container on the IC.
- 3.2.22 Postcolumn derivatization reagent (2.0 mM DPC in 90:10 1 N H_2SO_4 :methyl alcohol): In a 100-mL volumetric flask place 0.5 g of DPC fill to the mark with methyl alcohol and mix well. In a 1-L volumetric flask place about 500 mL deionized water, add 28 mL concentrated sulfuric acid, mix well, and allow to cool to room temperature. When the sulfuric acid solution is at room temperature, add the DPC/methanol solution, bring up to the mark with deionized water, mix well, and allow to cool to room temperature before placing in the postcolumn reservoir. This solution must be at room temperature for the complete reaction between DPC and Cr(VI). This solution is stable for 3 days. For the most sensitivity, this solution must be freshly prepared and be at room temperature.

3.3 Standard preparation

- 3.3.1 Wash all glassware in hot water with detergent, rinse with tap water, followed by deionized water, 10% nitric acid solution, and finally with two rinses of deionized water. **Under no circumstance should chromic acid cleaning be used.** It is best if glassware used for the analysis of Cr(VI) is reserved for this analysis only, so that the maximum sensitivity, and lack of outside interference can be obtained.
- 3.3.2 The stock standard solutions of 100 $\mu\text{g}/\text{mL}$ Cr(VI) are prepared by dissolving 0.2828 g of $\text{K}_2\text{Cr}_2\text{O}_7$ or 0.3735 g of K_2CrO_4 in 1 L of deionized water. (Prepare solution every 3 months.) Two separate stock solutions should be prepared, from separate sources, and used to make the dilutions. All dilutions of the stock solutions are made with DBE/PBM solution to obtain a working range of 0.3 to 500 ng/mL . Prepare dilutions monthly. (For example the stock calculation is: $(0.2828 \text{ g } \text{K}_2\text{Cr}_2\text{O}_7/\text{liter}) \times (1000 \text{ mg/g}) \times (1000 \text{ } \mu\text{g}/\text{mg}) \times (\text{L}/1000\text{mL}) \times (\text{MW Cr}/\text{MW } \text{K}_2\text{Cr}_2\text{O}_7 = 51.996/294.18) \times (2 \text{ moles of Cr in } \text{K}_2\text{Cr}_2\text{O}_7) = 100 \text{ } \mu\text{g}/\text{mL Cr(VI).}$)
- 3.3.3 Bracket sample concentrations with standard concentrations. If upon analysis, 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

- 3.4.1 Wash all glassware in hot water with detergent, rinse with tap water, deionized water, 10% nitric acid solution, and finally with two rinses of deionized water. **Under no circumstances should chromic acid cleaning be used.** If possible, this glassware should be reserved for the analysis of Cr(VI) only.
- 3.4.2 Adjust the hotplate temperature to below the boiling point of the BE solution, near 135 °C.
- 3.4.3 Remove the filter from the vial and place face or interior of the folds side down in a labeled 50-mL Erlenmeyer flask. Add 1.5 mL of PBM solution, swirl to wet the filter, then add 5 mL of BE solution and mix well before proceeding to the next sample. It is important to add the PBM solution first, as the freshly precipitated magnesium hydroxide that forms upon the addition of the BE solution, suppresses interference from the other metal ions. This precipitation happens immediately on mixing, so it is important that all sides of the filter be wetted. Heat the samples on the hotplate for 60 to 90 minutes, watching carefully to prevent the samples from boiling or evaporating to dryness. If the samples boil or evaporate to dryness the Cr(VI) will change to Cr(III) affecting the results.
- 3.4.4 Allow the samples to cool to room temperature. Quantitatively transfer each solution to a 10-mL volumetric flask using deionized water, and bring up to the mark with deionized water. Allow the samples to sit for 1 hour to allow the precipitate to settle, or centrifuge at 3200 rpm for 5 to 10 minutes. Carefully transfer the supernatant to the autosampler vial, and make sure that none of the precipitate is transferred. The precipitate will clog the IC.
- 3.4.5 For wipe samples of paints, a second extraction of the filter, with a stronger base solution, will be necessary to get the Cr(VI) out of the solidified paint. The two extractions are prepared separately, and analyzed separately. The analytical results of this second extraction are added to the first extraction to obtain the final result. Again add 1.5 mL of PBM solution to the Erlenmeyer flask, followed by the SPE solution, mix well and heat on the hotplate 60 to 90 minutes. Cool to room temperature, then quantitatively transfer the sample to a 25-mL volumetric flask with deionized water, and bring up to the mark with deionized water. Allow the samples to sit 1 hour to allow the precipitate to settle, or centrifuge at 3200 rpm for 5 to 10 minutes. Carefully transfer the supernatant to an autosampler vial.

3.5 Analysis

3.5.1 Analytical conditions

IC conditions	
columns:	IonPac AS7 column, 250-mm × 4-mm i.d. and IonPac NG-1 guard column 50-mm × 4-mm i.d. at ambient temperature
flow rate:	0.7 mL/min
eluent:	250 mM (NH ₄) ₂ SO ₄ with 100 mM NH ₄ OH
pump pressure:	~1000 psi
postcolumn derivatization solution:	~0.34 mL/min of 2.0 mM DPC in 90:10 of 1 N H ₂ SO ₄ :methyl alcohol
UV detector:	540 nm
injection size:	100 µL
retention time:	6.6 min
output range:	0.1 absorbance unit full scale (AUFS)
chromatogram:	Figure 3.5.1

3.5.2 An external standard (ESTD) calibration procedure is used to prepare a calibration curve using at least 2 stock standards, from separate sources, from which dilutions are made. The calibration curve is prepared daily. The samples are bracketed with analytical standards. (Figure 3.5.2)

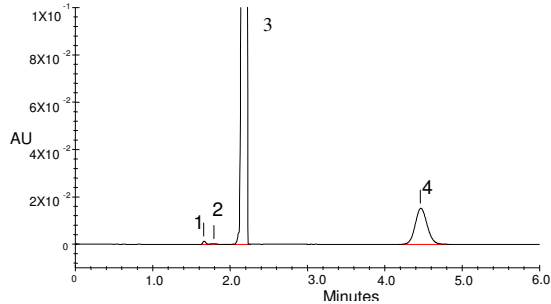


Figure 3.5.1. Chromatogram of an analytical standard of 50 ng/mL Cr(VI). (1 and 2 = solvent peaks, 3 = carbon dioxide from reaction of buffer and derivatizing solution, 4 = Cr(VI))

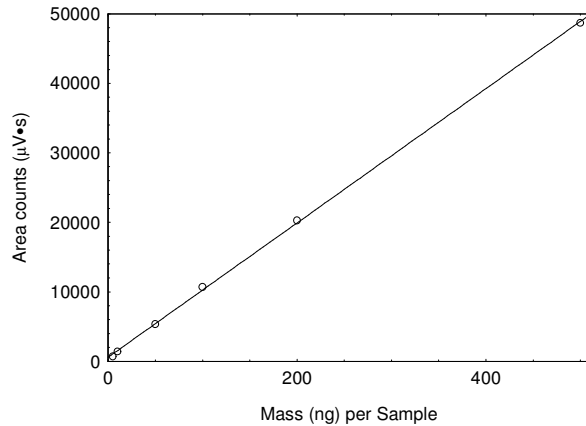


Figure 3.5.2. Calibration curve of Cr(VI). ($Y = 96.7X + 582$)

3.6 Interferences (analytical)

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

3.6.2 When necessary, the identity of an analyte peak may be confirmed with additional analytical data. The possibility of a coeluting species which does not react with the DPC, can be tested by injecting the sample with no postcolumn derivatizing agent being added.

3.6.3 The acid used in chrome plating operations is an interference.

3.7 Calculations

The amount of Cr(VI) per sampler is obtained from the appropriate calibration curve in terms of nanograms per sample, uncorrected for extraction efficiency. This amount is then adjusted by subtracting the amount (if any) found on the blank and corrected for extraction efficiency using the following formula. If samples were paint samples the results second extraction of the filter was also calculated with the following formula, then both results are added together.

$$M_s = \frac{(M - M_b)(C_f)}{E_e}$$

where M_s is the mass recovered from the sampled surface (μg)
 M is nanograms per sample
 M_b is the mass found on the blank (ng)
 E_e is extraction efficiency, in decimal form
 C_f is conversion factor of $\mu\text{g}/1000 \text{ ng}$

This amount may be expressed as μg Cr(VI) per 100 cm^2 if the surface area that was sampled was provided, by using the following formula.

$$C_s = \frac{100 \times M_s}{S}$$

where C_s is (μg) of Cr(VI) per 100 cm^2
 M_s is mass on the sampled surface (μg)
 S is surface area sampled (cm^2)
 100 cm^2 is one hundred cubic centimeters

The surface that was sampled may be less ideal (more porous, less smooth) than the surface that was used to evaluate the removal efficiency of the sampling media. In this circumstance, the media will remove the surface contaminant less effectively. There may be significant amounts of contaminant remaining on the surface after sampling. Nevertheless, the amount found in the sample indicates that at least this amount of Cr(VI) was present on the surface.

4. Backup Data

General background information about the determination of detection limits and reproducibility of the overall procedure is found in the "Evaluation Guidelines for Surface Sampling Methods".¹⁹ The Guidelines define analytical parameters, specific laboratory tests, statistical calculations and acceptance criteria.

4.1 Detection limit of the analytical procedure (DLAP)

The DLAP was calculated to be 90 picograms per injection. This is the lowest amount of analyte that will give a detector response that is significantly different from the response of a reagent blank. The standards were prepared in equally descending amounts of 100 picograms from 1000 to 0 picograms, such that the lowest standard had a peak at least ten times the baseline noise.

Table 4.1
Detection Limit of the Analytical Procedure

mass injected (pg)	area counts (μV-s)
0	0
100	215
200	386
300	509
400	629
500	728
600	831
700	960
800	1169
900	1295
1000	1428

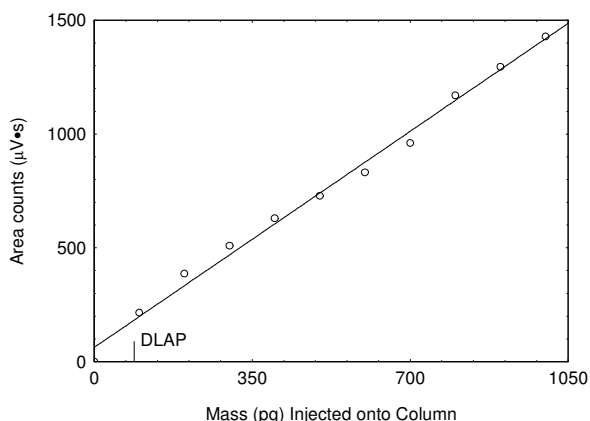


Figure 4.1. Plot of the data used to determine the DLAP ($Y = 1.36 X + 63$).

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

PVC filters

The DLOP is measured as mass per sample. Ten PVC filters were spiked with equal descending increments of analyte, such that the highest sampler loading was 10 ng/sample. These spiked samplers, and a sample blank were analyzed with the recommended analytical parameters, and the data obtained used to calculate the required parameters (standard error of estimate and the slope) for the calculation of the DLOP. Values of 131.6 and 40.0 were obtained for the slope and standard error of estimate respectively. The DLOP was calculated to be 0.911 ng/sample.

Table 4.2.1
Detection Limit of the Overall Procedure

mass per sample (ng)	area counts (μV-s)
0	0
1	209
2	379
3	498
4	615
5	710
6	806
7	938
8	1140
9	1256
10	1386

¹⁹ Lawrence, R. *Evaluation Guidelines for Surface Sampling Methods*; OSHA Salt Lake Technical Center, U.S. Department of Labor: Salt Lake City, UT, 2001, unpublished.

The RQL is considered the lower limit for precise quantitative measurements. It is determined from the regression line parameters obtained for the calculation of the DLOP, providing 75% to 125% of the analyte is recovered. The RQL is 3.04 ng per sample. Recovery at this concentration is 95.1%.

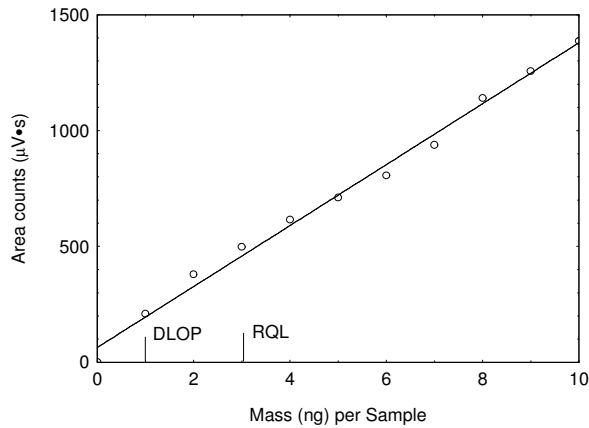


Figure 4.2.1. Plot of data to determine the DLOP/RQL for PVC filters. ($Y = 132X + 63.7$)

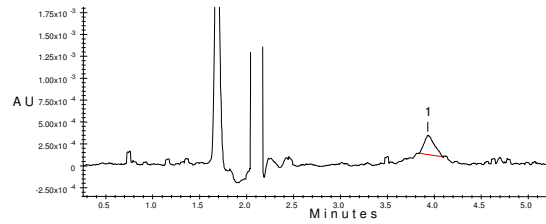


Figure 4.2.2. Plot of the RQL. (the large peaks that are off scale are carbon dioxide from the reaction of the buffer with the derivatizing solution. 1 = Cr(VI))

Binderless quartz fiber filters

The DLOP for the binderless quartz fiber filters was determined by spiking ten samplers with equal descending increments of analyte, such that the highest sampler loading was 10 ng/sample. These spiked samplers, and a sample blank were analyzed with the recommended analytical parameters, and the data obtained used to calculate the required parameters (standard error of estimate and the slope) for the calculation of the DLOP. Values of 137.2 and 56.0 were obtained for the slope and standard error of estimate respectively. The DLOP was calculated to be 0.67 ng/sample.

The RQL is considered the lower limit for precise quantitative measurements. It is determined from the regression line parameters obtained for the calculation of the DLOP, providing 75% to 125% of the analyte is recovered. The RQL is 2.23 ng per sample. Recovery at this concentration is 94.6%.

Table 4.2.2
Detection Limit of the Overall Procedure
Binderless Quartz Fiber Filter

mass per sample (ng)	area counts (µV·s)
0	0
1	201
2	376
3	491
4	602
5	712
6	813
7	943
8	1144
9	1255
10	1399

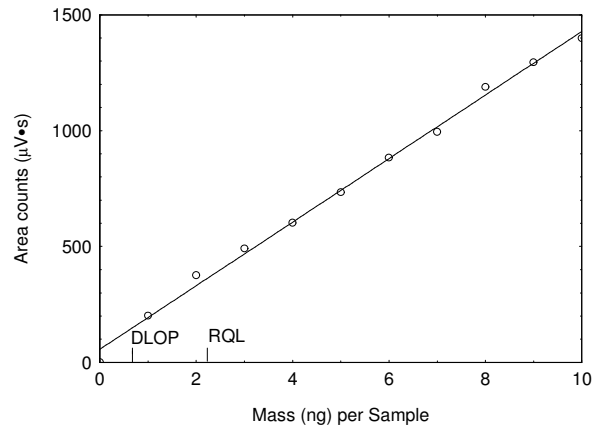


Figure 4.2.3. Plot of the data used to determine the DLOP/RQL for binderless quartz fiber filters ($Y = 137X + 56$).

1% NaOH Coated Binderless Quartz Fiber Filters

The DLOP for the 1% NaOH coated binderless quartz fiber filters was determined by spiking ten samplers with equal descending increments of analyte, such that the highest sampler loading was 10 ng/sample. These spiked samplers, and a sample blank were analyzed with the recommended analytical parameters, and the data obtained used to calculate the required parameters (standard error of estimate and the slope) for the calculation of the DLOP. Values of 138 and 87.1 were obtained for the slope and standard error of estimate respectively. The DLOP was calculated to be 0.937 ng/sample.

The RQL is considered the lower limit for precise quantitative measurements. It is determined from the regression line parameters obtained for the calculation of the DLOP, providing 75% to 125% of the analyte is recovered. The RQL is 3.12 ng per sample. Recovery at this concentration is 96.8%.

Table 4.2.3
Detection Limit of the Overall Procedure
1% NaOH coated Binderless Quartz Fiber
Filter

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

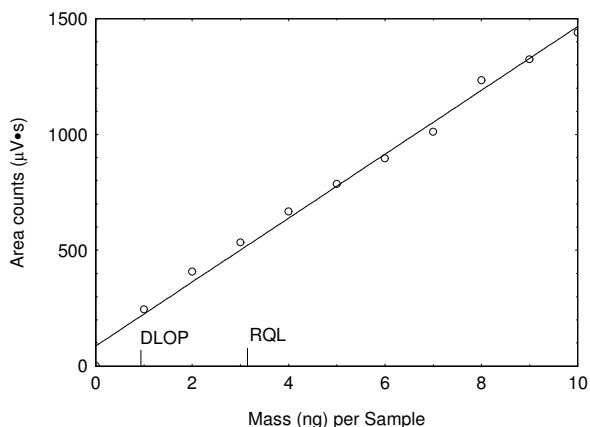


Figure 4.2.4. Plot of the data used to determine the DLOP/RQL for 1% NaOH coated binderless quartz fiber filters ($Y = 138 X + 87.1$).

4.3 Storage tests

Cr(VI) spiked on PVC filters

Storage samples were prepared by spiking PVC filters with Cr(VI). The PVC filter was spiked with the target concentration of Cr(VI) and allowed to dry. Twenty-one storage samples were prepared. 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 recoveries at Day 15 were 96.4% at ambient and refrigerated temperature.

Table 4.3.1
Storage Test for Cr(VI) on PVC Filters

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

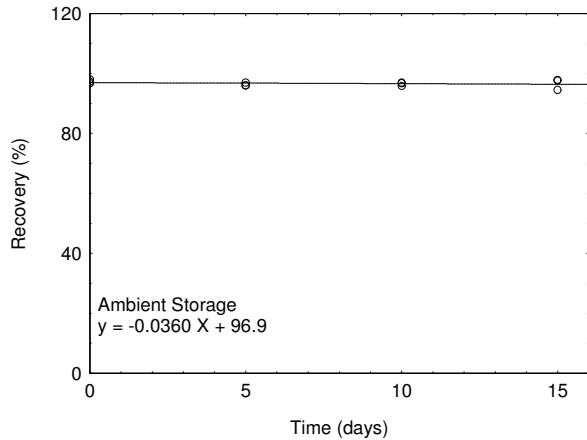


Figure 4.3.1. Ambient storage test for Cr(VI) spiked on PVC filters.

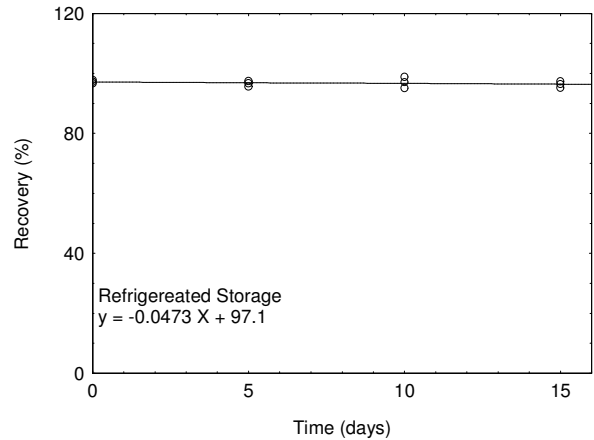


Figure 4.3.2. Refrigerated storage test for Cr(VI) spiked on PVC filters.

Cr(VI) spiked on binderless quartz fiber filters

Storage samples were prepared by spiking binderless quartz fiber filters with Cr(VI). The binderless quartz fiber filter was spiked with the target concentration of Cr(VI) and allowed to dry. Twenty-one storage samples were prepared. 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 recoveries at Day 15 were 96.4% at ambient temperature and 96.2% at refrigerated temperature.

Table 4.3.2
Storage Test for Cr(VI) on Binderless Quartz Fiber Filters

time (days)	ambient storage recovery (%)			refrigerated storage recovery (%)		
	0	98.2	98.1	97.1	98.2	97.1
5	97.9	96.1	96.7	97.1	97.9	96.7
10	96.1	96.6	97.2	97.3	98.2	96.1
15	97.3	97.2	95.1	96.1	96.3	95.3

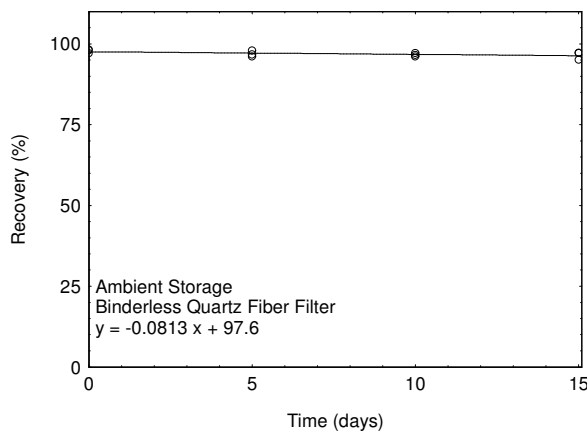


Figure 4.3.3. Ambient storage test for Cr(VI) spiked on binderless quartz fiber filters.

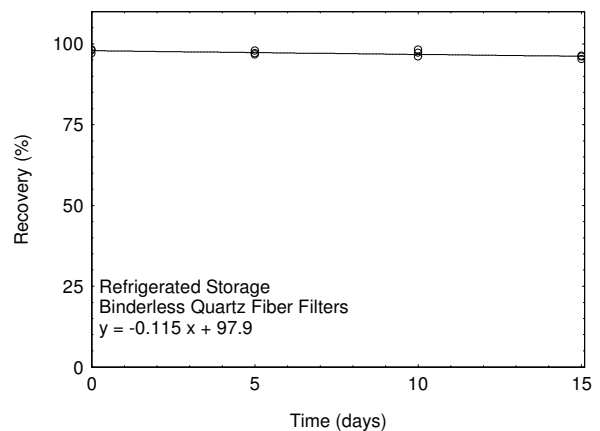


Figure 4.3.4. Refrigerated storage test for Cr(VI) spiked on binderless quartz fiber filters.

Cr(VI) and H₂SO₄ spiked on PVC filters

In chrome plating environments the presence of acid causes a negative interference due to reaction between the Cr(VI) and acid to form Cr(III). Most chrome plating baths contain H₂SO₄, so a mixture of H₂SO₄ and Cr(VI) was prepared in water to spike the filters with. Storage samples were prepared by spiking PVC filters with Cr(VI) and H₂SO₄. The PVC filter was spiked with 50 ng of Cr(VI) and 0.5 ng H₂SO₄ and allowed to dry. Twenty-one storage samples were prepared. 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. There was an immediate reaction between the Cr(VI) and the sulfuric acid, causing some of the Cr(VI) to change to Cr(III). Results were corrected for this bias. The results show a recovery of 78.0% on day 15 for samples stored at ambient temperature, and 81.0% for refrigerated samples.

Table 4.3.3
Storage Test for Cr(VI) and H₂SO₄ on PVC Filters

time (days)	ambient storage			refrigerated storage		
	recovery (%)			recovery (%)		
0	100.5	98.8	100.7	100.5	98.8	100.7
5	91.1	91.5	93.6	90.0	90.9	91.7
10	85.8	83.9	84.7	84.1	86.8	85.1
15	74.5	79.4	79.5	79.3	83.5	82.9

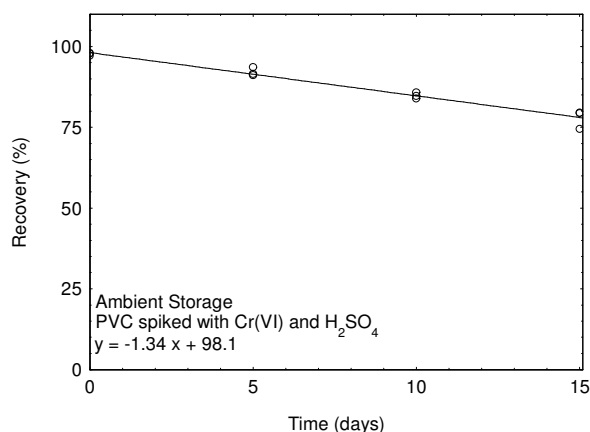


Figure 4.3.5. Ambient storage test for Cr(VI) and H₂SO₄ spiked on PVC filters.

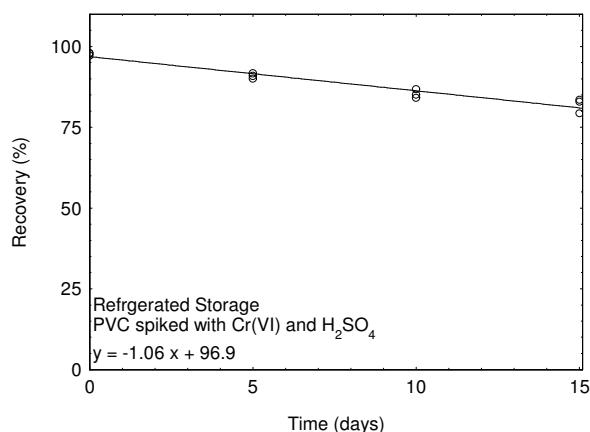


Figure 4.3.6. Refrigerated storage test for Cr(VI) and H₂SO₄ spiked on PVC filters.

Cr(VI) and H₂SO₄ spiked on PVC filters placed immediately in 5 mL of an aqueous solution containing 10% Na₂CO₃ with 2% NaHCO₃

The "Evaluation Guidelines for Surface Sampling Methods" states that a drop in recovery of greater than 10% upon storage for 15 days is a significant uncorrectable bias, and should be avoided.²⁰ The recoveries for the PVC filters spiked with Cr(VI) and H₂SO₄ on day 15 were 78.0% for ambient and 81.0% for refrigerated samples. To eliminate this negative bias from the H₂SO₄, the PVC filters were spiked with Cr(VI) and H₂SO₄ and then placed into a vial containing 5 mL of an aqueous solution containing 10% Na₂CO₃ with 2% NaHCO₃ (BE buffer) immediately. The PVC filter was spiked with 50 ng of Cr(VI) and 0.5 ng H₂SO₄. Twenty-one storage samples were prepared. 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

²⁰ Lawrence, R. *Evaluation Guidelines for Surface Sampling Methods*; OSHA Salt Lake Technical Center, U.S. Department of Labor: Salt Lake City, UT, 2001, unpublished.

analyzed. There was an immediate reaction between the Cr(VI) and the sulfuric acid, causing some of the Cr(VI) to change to Cr(III). Results were corrected for this bias. The recoveries on day 15 were 97.4% for ambient, and 98.0% for refrigerated.

Table 4.3.4
Storage Test for Cr(VI) and H₂SO₄ on PVC Filters and Placed in BE Buffer

time (days)	ambient storage recovery (%)			refrigerated storage recovery (%)		
	0	100.7	97.9	101.5	100.7	97.9
5	99.6	96.9	98.9	99.2	98.9	99.1
10	98.4	97.6	97.9	97.9	98.4	99.0
15	98.9	95.6	98.3	98.5	98.9	96.9

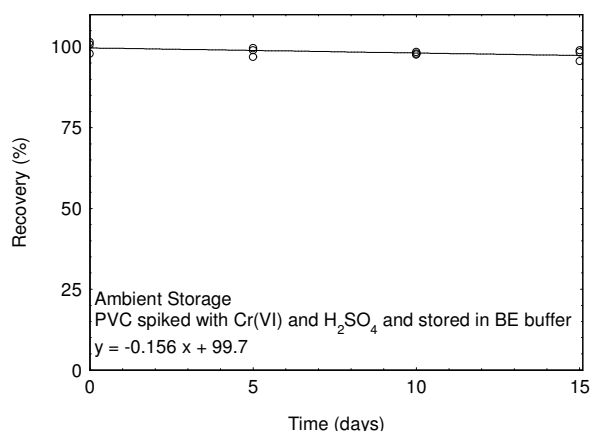


Figure 4.3.7. Ambient storage test for Cr(VI) and H₂SO₄ spiked on PVC filters and stored in 5 mL BE buffer.

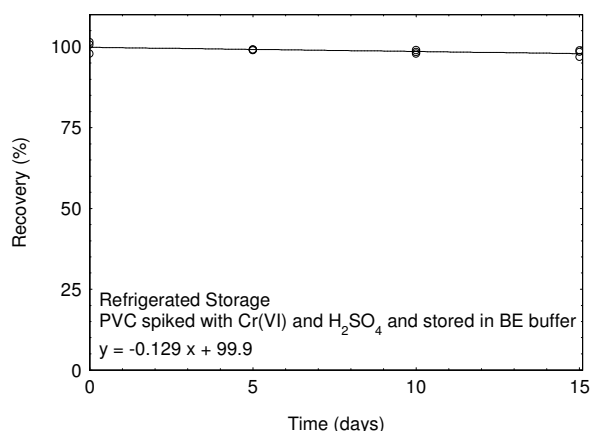


Figure 4.3.8. Refrigerated storage test for Cr(VI) and H₂SO₄ spiked on PVC filters and stored in 5 mL BE buffer.

Cr(VI) and H₂SO₄ spiked on binderless quartz fiber filters

Binderless quartz fiber filters were spiked with a mixture of H₂SO₄ and Cr(VI) in water at concentrations of 50 ng Cr(VI) and 0.5 ng H₂SO₄ and allowed to dry. Twenty-one storage samples were prepared. 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. There was an immediate reaction between the Cr(VI) and the sulfuric acid, causing some of the Cr(VI) to change to Cr(III). Results were corrected for this bias. The results show a recovery of 86.1% on day 15 for samples stored at ambient temperature, and 88.7% for refrigerated samples.

Table 4.3.5
Storage Test for Cr(VI) and H₂SO₄ on Binderless Quartz Fiber Filters

time (days)	ambient storage recovery (%)			refrigerated storage recovery (%)		
	0	100.9	99.3	99.8	100.9	99.3
5	94.8	93.0	95.1	96.4	93.2	95.4
10	90.1	91.2	89.9	93.7	92.2	93.4
15	85.4	86.8	86.1	87.9	89.2	87.3

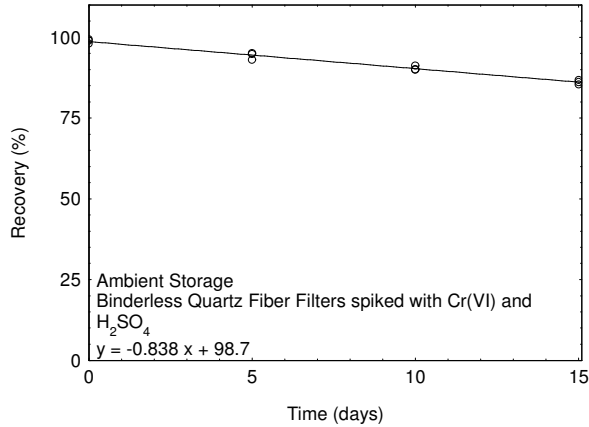


Figure 4.3.9. Ambient storage test for Cr(VI) and H₂SO₄ spiked on binderless quartz fiber filters.

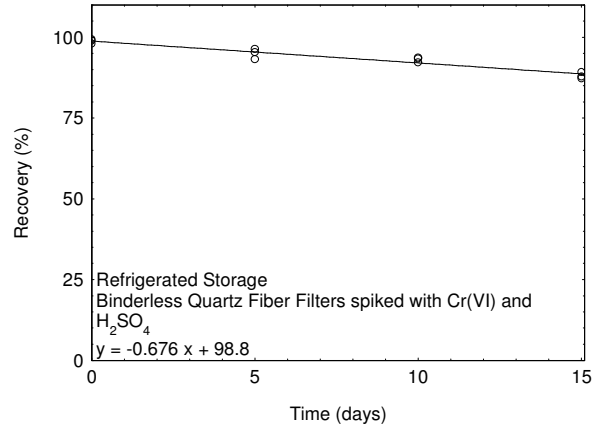


Figure 4.3.10. Refrigerated storage test for Cr(VI) and H₂SO₄ spiked on binderless quartz fiber filters.

Cr(VI) and H₂SO₄ spiked on binderless quartz fiber filter placed immediately in 5 mL of a solution containing 10% Na₂CO₃ with 2% NaHCO₃

Because the recoveries for the binderless quartz fiber filters spiked with the mixture of Cr(VI) and H₂SO₄ was 86.1% on day 15 for samples stored at ambient temperature, and 88.7% for refrigerated samples, placing the filters into 5 mL of an aqueous solution containing 10% Na₂CO₃ with 2% NaHCO₃ (BE buffer) immediately after spiking was performed. The binderless quartz fiber filter was spiked with 50 ng of Cr(VI) and 0.5 ng H₂SO₄. Twenty-one storage samples were prepared. 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. There was an immediate reaction between the Cr(VI) and the sulfuric acid, causing some of the Cr(VI) to change to Cr(III). Results were corrected for this bias. The recoveries on day 15 were 97.9% for ambient and 98.4% for refrigerated samples.

Table 4.3.6
Storage Test for Cr(VI) and H₂SO₄ on Binderless Quartz Fiber Filters and Placed in BE Buffer

time (days)	ambient storage			refrigerated storage		
	recovery (%)			recovery (%)		
0	100.8	99.9	99.3	100.8	99.9	99.3
5	96.9	97.9	98.9	98.8	97.9	99.3
10	98.4	98.5	97.9	97.9	98.9	98.5
15	98.3	97.5	97.6	99.1	98.1	97.9

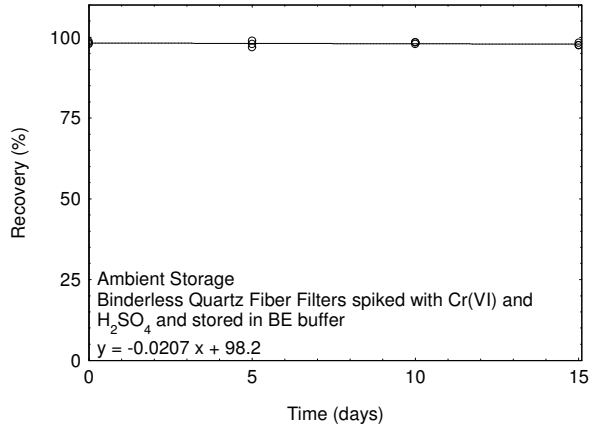


Figure 4.3.11. Ambient storage test for Cr(VI) and H₂SO₄ spiked on binderless quartz fiber filters and stored in 5 mL BE buffer.

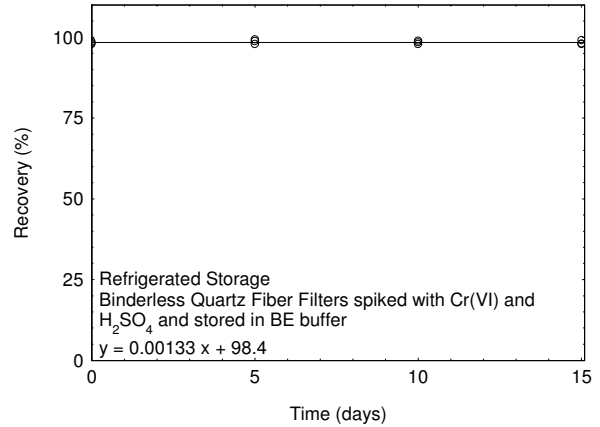


Figure 4.3.12. Refrigerated storage test for Cr(VI) and H₂SO₄ spiked on binderless quartz fiber filters and stored in 5 mL BE buffer.

Cr(VI) and H₂SO₄ spiked on 1% NaOH coated binderless quartz fiber filter

Storage samples were prepared by spiking 1% NaOH coated binderless quartz fiber filters with 50 ng Cr(VI) and 0.5 ng H₂SO₄ and allowed to dry. Twenty-one storage samples were prepared. 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. On Day 15 the recovery was 96.4% for samples stored at ambient temperature and 96.1% for samples stored at refrigerated temperature.

Table 4.3.7
Storage Test for Cr(VI) and H₂SO₄ on 1% NaOH Coated Binderless Quartz Fiber Filters

time (days)	ambient storage			refrigerated storage		
	recovery (%)			recovery (%)		
0	100.3	99.2	99.4	100.3	99.2	99.4
5	97.7	99.6	100.3	99.5	97.7	98.1
10	98.3	98.4	98.4	98.6	95.7	97.9
15	94.9	97.4	96.1	96.4	95.4	96.1

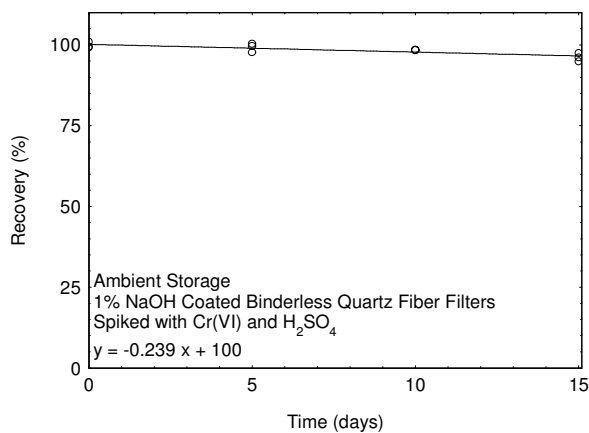


Figure 4.3.13. Ambient storage test for Cr(VI) and H₂SO₄ spiked on 1% NaOH coated binderless quartz fiber filters.

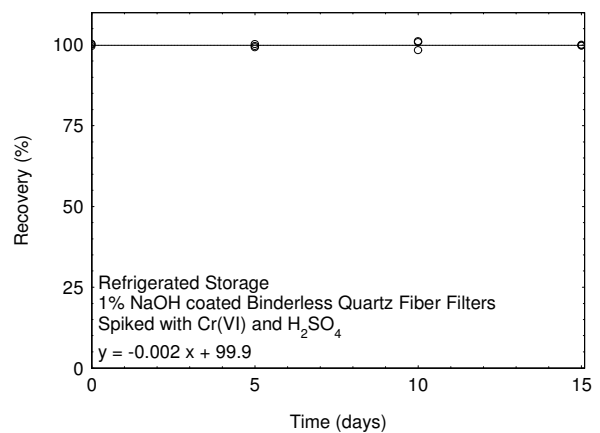


Figure 4.3.14. Refrigerated storage test for Cr(VI) and H₂SO₄ spiked on 1% NaOH coated binderless quartz fiber filters.

4.4 Sampler removal efficiency

4.4.1 Removal efficiency refers to the ability of the PVC filters to absorb or otherwise capture surface contaminants when the filter is moved across a surface under firm pressure. The surface used to evaluate the removal efficiency was a PTFE sheet. This type of surface approaches the smooth and non-porous characteristics of an ideal surface. The variety of surfaces found in workplaces will likely be less than ideal, so the media will have a lower removal efficiency. The amount of analyte found on the filter after sampling will indicate that at least that amount was present on the surface that was sampled. Six surfaces were spiked at the target concentration of Cr(VI), 0.05 µg/100 cm². Samples were collected from each surface using the technique described in Section 2.3 and analyzed. The results are shown in Table 4.4.1.

Table 4.4.1
Sampler Removal Efficiency
Data for Cr(VI) from PTFE using
PVC Filters

theoretical (µg/surface)	recovered (µg/sample)	recovery (%)
0.05	0.0490	98.0
0.05	0.0491	98.2
0.05	0.0488	97.6
0.05	0.0476	95.2
0.05	0.0479	95.8
0.05	0.0482	96.4

4.4.2 Removal efficiency of binderless quartz fiber filters was determined by placing the Cr(VI) on a PTFE sheet. This type of surface approaches the smooth and non-porous characteristics of an ideal surface. The variety of surfaces found in workplaces, including skin, will likely be less than ideal. The media will have a lower removal efficiency on less ideal surfaces. The amount of analyte found on the filter after sampling will indicate that at least that amount was present on the surface that was sampled. Six surfaces were spiked at the target concentration of Cr(VI), 0.05 µg/100 cm². Samples were collected from each surface using the technique described in Section 2.3 and analyzed. The results are shown in Table 4.4.2.

Table 4.4.2
Sampler Removal Efficiency Data for
Cr(VI) from PTFE using Binderless
Quartz Fiber Filters

theoretical (µg/surface)	recovered (µg/sample)	recovery (%)
0.05	0.0489	97.8
0.05	0.0493	98.6
0.05	0.0492	98.4
0.05	0.0483	96.6
0.05	0.0484	96.8
0.05	0.0489	97.8

4.4.3 Removal efficiency of 1% NaOH coated binderless quartz fiber filters was determined by placing the Cr(VI) on a PTFE sheet. This type of surface approaches the smooth and non-porous characteristics of an ideal surface. The variety of surfaces found in workplaces, including skin, will likely be less than ideal. The media will have a lower removal efficiency on less ideal surfaces. The amount of analyte found on the filter after sampling will indicate that at least that amount was present on the surface that was sampled. Six surfaces were spiked at the target concentration of Cr(VI), 0.05 µg/100 cm². Samples were collected from each surface using the technique described in Section 2.3 and analyzed. The results are shown in Table 4.4.3.

Table 4.4.3
Sampler Removal Efficiency Data for
Cr(VI) from PTFE using NaOH
Coated Binderless Quartz Fiber
Filters

theoretical (µg/surface)	recovered (µg/sample)	recovery (%)
0.05	0.0487	97.4
0.05	0.0493	98.6
0.05	0.0482	96.4
0.05	0.0483	96.6
0.05	0.0475	95.0
0.05	0.0491	98.2

4.4.4 Removal efficiency shall be calculated as follows:

$$E_R = \frac{A_R}{A_S}$$

where E_R is removal efficiency
 A_R is amount of analyte recovered
 A_S is amount of analyte spiked on the surface

The mean removal efficiency of the six samples was 96.9% for PVC filters, 97.7% for binderless quartz fiber filters, and 97.0% for 1% NaOH coated binderless quartz fiber filters..

4.5 Extraction efficiency

The extraction efficiencies of Cr(VI) were determined by liquid-spiking PVC filters with Cr(VI) at concentrations ranging from the RQL (0.06) to 10 times the target concentration. These samples were stored overnight at ambient temperature and then analyzed. The filters were either extracted and digested with the first, main extraction solution, BE, or with the second, spray paint only, SPE solution. The mean extraction efficiency over the working range of the RQL to 10 times the target concentration is 96.6% for samples extracted with the first (main) extraction solvent (BE) and 96.9% for samples extracted with the second extraction solvent for paint samples (SPE).

Table 4.5.1
 Extraction Efficiency of Cr(VI) from PVC Filters Extracted with BE

<u>level</u>		<u>sample number</u>				
× target concn	ng per sample	1	2	3	4	mean
RQL	3	95.4	96.6	92.7	95.5	95.1
0.1	5	96.4	96.5	97.9	95.9	96.7
1.0	50	97.8	97.2	96.7	97.6	97.3
10.0	500	97.4	97.8	97.0	96.1	97.1

Table 4.5.2
 Extraction Efficiency of Cr(VI) from PVC Filters Extracted with SPE

<u>level</u>		<u>sample number</u>				
× target concn	ng per sample	1	2	3	4	mean
RQL	3	97.8	95.0	97.3	95.5	96.4
0.1	5	97.5	97.1	97.6	96.0	97.1
1.0	50	95.9	97.5	96.3	96.1	96.5
10.0	500	98.0	96.4	97.1	97.9	97.4

The extraction efficiencies of Cr(VI) were determined by liquid-spiking binderless quartz fiber filters with Cr(VI) at concentrations ranging from the RQL (0.06) to 10 times the target concentration. These samples were stored overnight at ambient temperature and then analyzed. The filters were either extracted and digested with the first, main extraction solution, BE, or with the second, spray paint only, SPE solution. The mean extraction efficiency over the working range of the RQL to 10 times the target concentration is 97.3% for samples extracted with the first (main) extraction solvent (BE) and 96.2% for samples extracted with the second extraction solvent for paint samples (SPE).

Table 4.5.3
Extraction Efficiency of Cr(VI) from Binderless Quartz Fiber Filters Extracted with BE

<u>level</u>		<u>sample number</u>				mean
× target concn	ng per sample	1	2	3	4	
RQL	3	96.3	95.4	95.9	96.3	96.0
0.1	5	97.2	96.9	96.8	97.5	97.1
1.0	50	98.4	97.2	98.2	97.9	97.9
10.0	500	97.9	98.3	98.1	98.1	98.1

Table 4.5.4
Extraction Efficiency of Cr(VI) from Binderless Quartz Fiber Filters Extracted with SPE

<u>level</u>		<u>sample number</u>				mean
× target concn	ng per sample	1	2	3	4	
RQL	3	96.1	95.3	95.7	96.2	95.8
0.1	5	97.2	96.7	96.8	95.8	96.6
1.0	50	97.4	96.3	95.9	95.0	96.2
10.0	500	96.3	95.2	97.2	96.5	96.3

The extraction efficiencies of Cr(VI) were determined by liquid-spiking 1% NaOH coated binderless quartz fiber filters with Cr(VI) at concentrations ranging from the RQL (0.06) to 10 times the target concentration. These samples were stored overnight at ambient temperature and then analyzed. The filters were either extracted and digested with the first, main extraction solution, BE, or with the second, spray paint only, SPE solution. The mean extraction efficiency over the working range of the RQL to 10 times the target concentration is 97.3% for samples extracted with the first (main) extraction solvent (BE) and 96.9% for samples extracted with the second extraction solvent for paint samples (SPE).

Table 4.5.5
Extraction Efficiency of Cr(VI) from 1% NaOH Coated Binderless Quartz Fiber Filters Extracted with BE

<u>level</u>		<u>sample number</u>				mean
× target concn	ng per sample	1	2	3	4	
RQL	3	97.4	95.3	97.1	96.2	96.5
0.1	5	96.3	97.1	96.9	97.4	96.9
1.0	50	98.1	95.9	98.1	98.2	97.6
10.0	500	97.7	98.1	97.9	98.3	98.0

Table 4.5.6
Extraction Efficiency of Cr(VI) from 1% NaOH Coated Binderless Quartz Fiber Filters Extracted with SPE

<u>level</u>		<u>sample number</u>				mean
× target concn	ng per sample	1	2	3	4	
RQL	3	96.9	95.9	96.3	95.4	96.1
0.1	5	98.1	96.8	97.7	95.4	97.0
1.0	50	97.9	97.5	96.8	96.5	97.2
10.0	500	96.9	97.2	97.9	97.5	97.4

4.6 Reproducibility

- 4.6.1 Six PTFE surfaces were spiked at the target level of 50 ng Cr(VI). A chemist, other than the one developing the method, conducted sampling on the PTFE surfaces as described in Section 2 using PVC filters. The test was repeated with a second chemist performing the sampling. The samples were analyzed. The first chemist was able to achieve a removal efficiency of 96.0% and the second chemist 95.1% (Tables 4.6.1.1 and 4.6.1.2).

Table 4.6.1.1
Sampling Reproducibility
1st Chemist Samples for Cr(VI) from
PTFE using PVC Filters

theoretical (ng/surface)	recovered (ng/sample)	recovery (%)
50	48.2	96.4
50	48.7	97.4
50	48.4	96.8
50	47.2	94.4
50	48.3	96.6
50	47.2	94.4

Table 4.6.1.2
Sampling Reproducibility
2nd Chemist Samples for Cr(VI) from PTFE
using PVC Filters

theoretical (ng/surface)	recovered (ng/sample)	recovery (%)
50	46.5	93.0
50	47.9	95.8
50	48.6	97.2
50	48.7	97.4
50	46.9	93.8
50	46.7	93.4

- 4.6.2 Six samples were prepared by spiking PVC filters in the same manner that was used in the preparation for the storage study. The samples were submitted to the OSHA SLTC for analysis. The samples were analyzed after being stored for 13 days at 23 °C. Sample results were corrected for extraction efficiency. The average recovery was 97.6%.

Table 4.6.2
Analytical Reproducibility
Data for Cr(VI) using PVC Filters

theoretical (ng/surface)	recovered (ng/sample)	recovery (%)
50	48.1	96.2
50	49.2	98.4
50	47.9	95.8
50	48.6	97.2
50	49.1	98.2
50	49.8	99.6

- 4.6.3 Six PTFE surfaces were spiked at the target level of 50 ng Cr(VI). A chemist, other than the one developing the method, conducted sampling on the PTFE surfaces as described in Section 2 using binderless quartz fiber filters. The test was repeated with a second chemist performing the sampling. The samples were analyzed. The first chemist was able to achieve a removal efficiency of 95.9% and the second chemist 96.0% (Tables 4.6.3.1 and 4.6.3.2).

Table 4.6.3.1
Sampling Reproducibility
1st Chemist Samples for Cr(VI) from
PTFE using Binderless Quartz Fiber
Filters

theoretical (ng/surface)	recovered (ng/sample)	recovery (%)
50	47.2	94.4
50	48.9	97.8
50	47.1	94.2
50	47.5	95.0
50	48.8	97.6
50	48.4	96.8

Table 4.6.3.2
Sampling Reproducibility
2nd Chemist Samples for Cr(VI) from
PTFE using Binderless Quartz Fiber
Filters

theoretical (ng/surface)	recovered (ng/sample)	recovery (%)
50	47.5	95.0
50	48.6	97.2
50	48.3	96.6
50	48.8	97.6
50	47.1	94.2
50	47.7	95.4

4.6.4 Six samples were prepared by spiking binderless quartz fiber filters in the same manner that was used in the preparation for the storage study. The samples were submitted to the OSHA SLTC for analysis. The samples were analyzed after being stored for 5 days at 23 °C. Sample results were corrected for extraction efficiency. The average recovery was 96.5%.

Table 4.6.4
Analytical Reproducibility
Data for Cr(VI) using Binderless Quartz
Fiber Filters

theoretical (ng/surface)	recovered (ng/sample)	recovery (%)
50	47.3	94.6
50	48.4	96.8
50	47.9	95.8
50	48.2	96.4
50	48.8	97.6
50	48.9	97.8

4.6.5 Six PTFE surfaces were spiked at the target level of 50 ng Cr(VI). A chemist, other than the one developing the method, conducted sampling on the PTFE surfaces as described in Section 2 using 1% NaOH coated binderless quartz fiber filters. The test was repeated with a second chemist performing the sampling. The samples were analyzed. The first chemist was able to achieve a removal efficiency of 96.0% and the second chemist 96.5% (Tables 4.6.5.1 and 4.6.5.2).

Table 4.6.5.1
Sampling Reproducibility
1st Chemist Samples for Cr(VI) from
PTFE using NaOH Coated Binderless
Quartz Fiber Filters

theoretical (ng/surface)	recovered (ng/sample)	recovery (%)
50	47.9	95.8
50	47.8	95.6
50	48.2	96.4
50	48.7	97.4
50	47.9	95.8
50	47.5	95.0

Table 4.6.5.2
Sampling Reproducibility
2nd Chemist Samples for Cr(VI) from PTFE
using 1% NaOH Coated Binderless Quartz
Fiber Filters

theoretical (ng/surface)	recovered (ng/sample)	recovery (%)
50	48.9	97.8
50	47.2	94.4
50	47.7	95.4
50	48.8	97.6
50	48.9	97.8
50	47.9	95.8

4.6.6 Six samples were prepared by spiking 1% NaOH coated binderless quartz fiber filters in the same manner that was used in the preparation for the storage study. The samples were submitted to the OSHA SLTC for analysis. The samples were analyzed after being stored for 9 days at 23 °C. Sample results were corrected for extraction efficiency. The average recovery was 95.8%.

Table 4.6.6
Analytical Reproducibility
Data for Cr(VI) on NaOH Coated
Binderless Quartz Fiber Filters

theoretical (ng/surface)	recovered (ng/sample)	recovery (%)
50	47.4	94.8
50	48.2	96.4
50	48.8	97.6
50	47.1	94.2
50	47.6	95.2
50	48.4	96.8

4.7 Interferences (sampling)

Suspected interferences should be reported to the laboratory with submitted samples. The interference studies were performed in Method ID-215 Hexavalent Chromium, and should be consulted for specific information about the metal species of interest²¹. The major positive interference is Cr(III), which can be oxidized to Cr(VI). The major negative interference is Fe(II), which can reduce the Cr(VI) to Cr(III). Other reducing metal species can also change Cr(VI) to Cr(III).

²¹ Ku, J., Eide, M., ID-215 Hexavalent Chromium, 1998, <http://www.osha.gov>, (accessed May 2000)

In chrome plating operations the acid is a negative interference, and samples taken on PVC or uncoated binderless quartz fiber filters must be placed into a vial containing a solution of 10% Na₂CO₃ with 2% NaHCO₃, or the 1% NaOH coated binderless quartz fiber filters should be used.

4.8 Confirmation

The presence of Cr(VI) can be confirmed by a second column analysis using a different column packing, ICP-mass spec, or by reanalyzing the samples without the addition of the postcolumn derivatizing solution. To confirm the sample without the addition of the post column derivatizing solution, a solution of 90:10 0.1 N H₂SO₄:methyl alcohol is substituted for the derivatizing solution, and the sample is rerun under the same conditions it was first analyzed under. If a peak appears at the same retention time as the hexavalent chromium, it is an interference, but conversely, if no peak appears, the original peak was all hexavalent chromium.

4.9 Preparation of the 1% NaOH coated binderless quartz fiber filters

The 1% NaOH coated binderless quartz fiber filters are prepared by placing binderless quartz fiber filters in a single layer in a shallow pan containing 1 N NaOH overnight. They were removed and placed on a PTFE sheet to dry for four hours. Twelve dry filters were placed into a sealed jar and stored for up to 60 days, and another twelve dry filters were placed into a jar, a stream of nitrogen was blown into the jar for 1 minute to blanket the filters, and then sealed and stored for up to 67 days. The filters were analyzed by acid titration after 29 and 67 days to determine the available hydroxide ion. The filters stored under nitrogen stored the best, with recoveries of 95.6% for 29 days and 90.8% for 67 days. Filters stored with air were barely acceptable for 29 days, 84.0% recovery, but those stored for 67 days lost too much of the hydroxide ion, 65.6% recovery. These results indicate that the filters should be used within a month of preparation, unless they are stored under nitrogen, then they can be stored two months.

Table 4.9
Storage of 1% NaOH coated Binderless Quartz Fiber Filter

<u>Filter Storage</u>		<u>sample number</u>				
type of gas over filters	days stored	1	2	3	4	mean
air	30	83.2	85.4	84.9	82.8	84.0
air	60	63.0	68.6	64.5	66.3	65.6
nitrogen	30	95.4	96.6	94.9	95.4	95.6
nitrogen	60	90.2	90.9	90.6	91.4	90.8