

Field test of a portable method for the determination of hexavalent chromium in workplace air

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Hexavalent chromium, Cr(VI), is a human carcinogen that may be present in the workplace air of a variety of occupational settings.¹ Occupational exposure to Cr(VI) has been associated with a number of work activities, including metal plating, welding, spray painting, tanning, and abrasive blasting operations.² Recent efforts in the authors' laboratory have been directed toward the development and evaluation of field-portable methods for the on-site measurement of Cr(VI) and other toxic metals in workplace air and other environmental matrices. Various analytical methods are in existence for the determination of airborne Cr(VI) in fixed-site laboratories with conventional laboratory instrumentation,³⁻⁷ but reliable field-portable methods are needed for on-site occupational monitoring of this species. Field-portable methods are often desired so that decisions regarding worker protection, engineering controls, etc., can be made quickly. The capability for rapid decision-making based on field analysis results can help to save costs, and also offers a means to assess (and thereby prevent) worker overexposures to hexavalent chromium in a timely manner.

A field-portable analytical method for measuring Cr(VI) in environmental and workplace air samples has been developed.⁸ This method employs alkaline ultrasonic extraction of Cr(VI) from environmental and filter media using an ammonium sulfate/ammonium hydroxide buffer solution (pH 8).⁹ This buffer helps to stabilize hexavalent and trivalent chromium in solution, thereby preventing reduction of Cr(VI) or oxidation of Cr(III).¹⁰ Following ultrasonic extraction, hexavalent chromium is separated from trivalent chromium and other cations by solid-phase extraction using a strong anion exchange resin (quaternary amine bound to silica). Isolated Cr(VI) is then eluted with ammonium sulfate/ammonium hydroxide buffer from the anion exchange column, complexed with 1,5-diphenylcarbazide (DPC), and measured by visible absorption spectrophotometry with a field-portable, battery-powered instrument. This procedure was found to give excellent recoveries for insoluble Cr(VI).^{8,9} The method is simple, rapid, sensitive, and quantitative, and provides the ability for on-site workplace exposure monitoring. Analytical results are obtained within 2 hr of sampling.

In this study, a portable spectrophotometer and a portable solid-phase extraction manifold were transported to the field, and the Cr(VI) portable analytical method was field tested at a facility at which aircraft were being refurbished. An industrial hygiene survey was conducted during sanding and spray-painting operations, and air samples were collected and analyzed for Cr(VI) on-site. Some area air samples were collected above an electroplating bath where galvanizing of airplane parts was conducted. Three types of membrane filters were used in order to compare analytical results from the different filter media. Presented herein are the results from this industrial hygiene survey using the field-portable method for the determination of Cr(VI) in workplace air.

Experimental

Sample collection

Air samples were collected using 37-mm-diam filters housed in polystyrene cassettes, with the air inlet enlarged to 15 mm in order to simulate the Institute of Occupational Medicine (IOM) samplers for inhalable particulate mass.¹¹ The three different

types of membrane filters used were: 1) polyvinyl chloride (PVC) (5.0 μm pore size), 2) mixed cellulose ester (MCE) (0.8 μm pore size), and 3) polytetrafluoroethylene (PTFE) (1.0 μm pore size). All filter media were obtained from SKC (Eighty Four, PA). Personal breathing zone (PBZ) as well as area air samples were collected for the length of time required to complete the tasks of interest using Gil Air 3 sampling pumps (Sensidyne, Clearwater, FL) calibrated to an airflow rate of 2.0 ± 0.1 L/min. Area samples were collected side by side so that results from different filter types could be compared. All air samples were collected during aircraft refurbishing operations.

Materials and equipment for analysis

The air samples were analyzed for Cr(VI) on the same day they were collected, at the facility at which they were obtained. Sample analysis was conducted using the following chemicals (reagent grade), which were purchased from Aldrich (Milwaukee, WI): Cr(VI) 1005 $\mu\text{g}/\text{mL}$ standard; ammonium sulfate (NH_4)₂SO₄, ammonium hydroxide, NH₄OH; 1,5-diphenylcarbazide (DPC); acetonitrile; and 37% hydrochloric acid (HCl). Ultrasonic extraction of air filters was performed using a Sonicor 115-V, 60-Hz sonicator (Sonicor, Farmingdale, NY). Solid-phase extraction (SPE) of ultrasonicated extracts was performed using a Supelclean™ solid-phase extractor (Supelco, Bellefonte, PA) attached to a vacuum pump (Gast, Benton Harbor, MI) via a pressure metering valve. Strong anion exchange (SAE) cartridges (Supelco), tube size 3 mL, consisted of 500 mg of quaternary amine-bonded silica sorbent with Cl⁻ as the counterion (capacity 0.2 meq/g). A DR/2010 portable spectrophotometer (Hach, Loveland, CO) was used for spectrophotometric measurements at 540 nm (sample path length 1 cm).

Ultrasonic extraction of filter samples

Following sample collection, filters were removed from the sampling cassettes and placed in 15-mL plastic centrifuge tubes with screw caps (Becton Dickinson, Franklin Lakes, NJ). Then 10 mL of 0.05 M ammonium sulfate/0.05 M ammonium hydroxide buffer solution (pH 8) was introduced into the centrifuge tubes containing the membrane filters. The immersed filter samples were then sonicated in the ultrasonic bath for 30 min at a temperature of 34–40 °C. PBZ and area samples were treated in the same fashion.

Solid-phase extraction

SAE cartridges were placed in the inlet ports of the SPE manifold and conditioned by drawing (via vacuum) 3 mL of doubly-distilled water through the cartridges. Thereafter, 3-mL aliquots of the sample solutions (which had been sonicated) were pipetted from the centrifuge tubes into the SAE cartridges. After sample loading, the cartridges were again rinsed with 3 mL of doubly distilled water, and the rinsates discarded. In this manner, Cr(VI), which is anionic at pH < 10, was loaded onto the ion exchange sorbent within the cartridges, while Cr(III) and other cations were unretained on the cartridges. Hexavalent chromium was eluted with 6 mL of 0.5 M ammonium sulfate/0.05 M ammonium hydroxide buffer solution in two 3-mL fractions at a flow rate of 2 mL/min; eluates were collected in 20-mL scintillation vials.

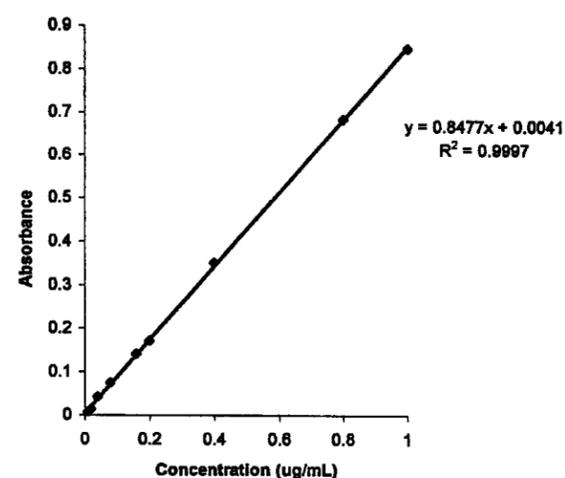


Figure 1 Representative calibration line of hexavalent chromium concentration (measured as the chromium-diphenylcarbazide complex) versus absorbance (in absorbance units) at 540 nm using a portable, battery-powered spectrophotometer.

Table 1
Area Cr(VI) concentrations determined from air samples collected during aircraft refurbishing activities*

Cr(VI) concentrations, $\mu\text{g}/\text{m}^3$		
PVC	MCE	PTFE
48.7	52.7	37.4
68.7	73.8	37.8
129	105	62.3
8.19	10.3	6.49
11.2	5.10	11.9
8.67	7.00	14.2
1430	1370	1510
141	139	—
1680	1650	—
12.0	11.0	33.8
19.1	13.9	28.6
1.43	19.3	—
72.5	73.0	62.1
34.5	92.9	63.3
78.6	138	136
62.6	62.6	45.2
145	—	242

*Samples were collected side by side on PVC, MCE, and PTFE filters during sanding, spray-painting, and electroplating operations.

Spectrophotometric measurement

Eluate solutions containing isolated Cr(VI) were acidified with 100 μL of 37% hydrochloric acid, followed by the addition of 2 mL of 20 mM DPC (in acetonitrile) complexing reagent solution to the eluates. Quantification of Cr(VI) concentrations was performed by measuring the absorbance due to the Cr-DPC complex at 540 nm using the portable spectrophotometer. Calibration solutions consisting of known concentrations of Cr(VI) were prepared by dilution of the 1005 $\mu\text{g}/\text{mL}$ Cr(VI) standard, and these solutions were used to prepare calibration lines from which Cr(VI) concentrations in the filter samples (as prepared above) could be determined. Concentrations of calibration solutions ranged from 0.01 to 1 μg Cr(VI)/mL.

Results and discussion

Figure 1 shows the calibration line of absorbance at 540 nm (due to the Cr-DPC complex) as a func-

Table 2
Statistical comparisons for Cr(VI) area air samples collected side by side during aircraft refurbishing operations on PVC, MCE, and PTFE filters*

(A) PVC vs MCE (n = 16)
Mean: PVC = 238.2 µg/m³; MCE = 239.0 µg/m³
Variance: PVC = 269089; MCE = 250628
 $t = 0.0955$; critical t (15 degrees of freedom) = 1.7531

(B) PVC vs PTFE (n = 14)
Mean: PVC = 152.2 µg/m³; PTFE = 163.9 µg/m³
Variance: PVC = 137626; PTFE = 154466
 $t = 1.0092$; critical t (13 degrees of freedom) = 1.7709

(C) MCE vs PTFE (n = 13)
Mean: MCE = 155.3 µg/m³; PTFE = 157.9 µg/m³
Variance: MCE = 135729; PTFE = 167001
 $t = 0.2013$; critical t (12 degrees of freedom) = 1.7823

*The statistics applied were paired two-sample, two-sided t -tests for means ($\alpha = 0.1$).

tion of Cr(VI) concentration. The figure shows typical calibration data from standards analyzed on-site using the field-portable spectrophotometer following solid-phase extraction. The response is linear over a wide concentration range (0.01–1.00 µg Cr(VI)/mL; $R^2 = 0.9997$). The NIOSH Standard Operating Procedure (SOP) 018¹² was used to estimate the detection limit for Cr(VI). A detection limit of 0.08 µg Cr(VI) per sample was determined,⁸ yielding a method detection limit of less than 0.1 µg/m³ for an 8-hr time-weighted average (TWA) when sampling at 2 L/min. For comparison, the Threshold Limit Value (TLV) for insoluble Cr(VI) is 10 µg/m³.¹³ Thus, the method is useful for occupational exposure monitoring, since the detection limit is more than an order of magnitude less than the action level of interest.¹²

It was desired to compare analysis results for samples that were collected on different filter media. Table 1 shows results for area air samples for the three different filter types; these samples were collected side by side during different work activities or processes (i.e., sanding, spray painting, and electroplating). Statistical treatment of results from comparing MCE and PVC filters are shown in Table 2A, statistical comparison data for PVC and PTFE filters are given in Table 2B, and MCE versus PTFE analysis results are presented in Table 2C. In each of the three cases, there is no statistically significant difference between the analytical results obtained for the different types of filters. This is evidenced by the calculated t -statistic being less than the critical t -value for each of the three instances in which the different filter types were compared against one another (see Table 2). These results indicate that for same-day sampling and analysis, any of the three filter types is acceptable for Cr(VI) workplace exposure monitoring. Most methods for Cr(VI) occupational monitoring (e.g., NIOSH,³ HSE,⁴ and OSHA⁵) specify PVC filters for sample collection, since other types of filters are known to cause Cr(VI) reduction.^{5,14} However, as this reduction apparently occurs on a slow time scale,¹⁴ other filter types besides PVC may be acceptable for same-day field sampling and analysis.

Table 3 shows results for personal monitoring of Cr(VI) for different work tasks during aircraft refurbishing operations. Hexavalent chromium samples were obtained within the personal breathing zones of workers who were performing the different work activities (e.g., priming, painting, and sanding). The highest exposures were found for priming; this was not unexpected, due to the presence of chromate in the primer coating. The lowest exposures were found for overcoating with a gray-colored paint, which contained no chromate. Intermediate exposures were observed for sanding activities. Keeping in mind that the TLV for insoluble Cr(VI) is 10 µg/m³, it can be seen from the data in Table 3 that personal protection and/or engineering controls are needed for several work activities, since Cr(VI) con-

Table 3
PBZ Cr(VI) concentrations measured in air samples collected during aircraft sanding and spray-painting operations

Task description	n	Mean [Cr(VI)] (µg/m ³)	SD	Min. [Cr(VI)] (µg/m ³)	Max. [Cr(VI)] (µg/m ³)
All PBZ samples	44	89.2	187	3.09	1146
Spray painting (overcoating)	3	ND*	—	ND	ND
Primer spray painting (aircraft A)	7	134	87.9	50.1	315
Primer spray painting (aircraft B)	8	75.2	336	31.2	1146
Sanding (aircraft A)	12	23.4	27.0	3.09	96.8
Sanding (aircraft B)	14	13.9	9.52	3.32	42.6

*ND: none detected (detection limit = 0.10 µg/m³).

Table 4
Cr(VI) concentrations determined in area air samples collected during aircraft sanding and spray-painting operations

Task description	n	Mean [Cr(VI)] (µg/m ³)	SD	Min. [Cr(VI)] (µg/m ³)	Max. [Cr(VI)] (µg/m ³)
All area samples	37	37.4	32.8	1.43	129
Spray painting (overcoating)	3	ND*	—	ND	ND
Primer spray painting (aircraft A)	18	39.3	27.4	1.43	92.9
Primer spray painting (aircraft B)	9	68.3	29.0	37.4	129
Sanding (aircraft B)	7	8.70	3.77	2.61	14.2

*ND: none detected (detection limit = 0.10 µg/m³).

centrations above the TLV were observed in numerous instances.

Results for area air samples are shown in Table 4; these results illustrate generally lower Cr(VI) exposures than do the personal monitoring results (Table 3). This is probably due to sampling further from the source, as area samples were collected in the vicinity of the work environment, but in a manner that did not impede work activities. Similar trends in Cr(VI) concentrations were observed for the area air samples as for personal air samples, i.e., the highest levels were found for priming, the lowest for overcoating, and intermediate exposures were seen for sanding operations (Table 4).

The data shown in Tables 3 and 4 suggest that on-site monitoring in the field can give useful information regarding Cr(VI) exposures for different work activities where excessive hexavalent chromium exposures may occur. Information concerning Cr(VI) exposures within 2 hr of sampling can provide for immediate corrective action, if needed. Also, same-day data analysis can allow for short-term workplace compliance monitoring, and may reduce costs due to job downtime that might otherwise occur while awaiting analytical results from off-site laboratory analysis.

Conclusion

The results from this field study demonstrate that Cr(VI) air samples can be collected and analyzed on-site immediately following sample collection. Approximately 2 hr are needed to prepare and analyze calibration standards and to analyze Cr(VI) in a dozen air filter samples, with the limiting factor being the number of ports for the SAE cartridges in the SPE manifold. The results show that the field method is useful for industrial hygiene purposes, since it is sensitive and accurate enough to measure Cr(VI) concentrations well below the TLV. The method can be used to assess Cr(VI) exposures for different work practices, and offers potential for both short-term and full-shift exposure monitoring. Furthermore, reduction of Cr(VI) to Cr(III) does not appear to be a problem when using MCE, PTFE, or PVC filters for sample collection when analysis is performed the same day samples are collected.

References

- Chromium in the natural and human environments. In: Nragu JO, Nieboer E, eds. New York: Wiley, 1988.
- NIOSH. Criteria for a recommended standard—occupational exposure to chromium(VI). Cincinnati, OH: National Institute for Occupational Safety and Health, 1975.

- NIOSH manual of analytical methods, 4th ed., method nos. 7600 and 7604. In: Eller PM, Cassinelli ME, eds. Cincinnati, OH: National Institute for Occupational Safety and Health, 1994.
- Health and Safety Laboratory/HSE. Methods for the determination of hazardous substances, MDHS method no. 61. Sheffield, UK: Health and Safety Executive, 1998.
- OSHA, Hexavalent chromium in workplace atmospheres, method no. ID-215. Salt Lake City, UT: Occupational Safety and Health Administration, 1998.
- ASTM D5281, Standard test method for collection and analysis of hexavalent chromium in ambient, workplace, or indoor atmospheres. Annual book of ASTM standards, vol. 11.03. Philadelphia, PA: American Society for Testing and Materials, 1996.
- U.S. EPA, Hexavalent chromium: colorimetric method, method no. 7196. Cincinnati, OH: U.S. Environmental Protection Agency, 1984.
- Wang J, Ashley K, Marlow D, England E, Carlton G. Field method for the determination of hexavalent chromium by ultrasonication and strong anion exchange solid phase extraction; *Anal Chem* 1999; 71:1027–32.
- Wang J, Ashley K, Kennedy ER, Neumeister C. Determination of hexavalent chromium in industrial hygiene samples using ultrasonic extraction and flow injection analysis. *Analyst* 1997; 122:1307–12.
- Sheehan P, Ricks R, Ripple S, Paustenbach D. Field evaluation of a sampling and analytical method for environmental levels of airborne hexavalent chromium. *Am Ind Hyg Assoc J* 1992; 53:57–68.
- Bartley DL. Inhalable aerosol samplers. *Appl Occup Environ Hyg* 1998; 13:274–8.
- Kennedy ER, Fischbach TJ, Song R, Eller PM, Shulman SA. Guidelines for air sampling and analytical method development and evaluation. Cincinnati, OH: National Institute for Occupational Safety and Health, 1995.
- ACGIH. Threshold limit values for chemical substances and physical agents; biological exposure indices. Cincinnati, OH: American Conference of Government Industrial Hygienists, 1998.
- Molina D, Abell M. An ion chromatographic method for insoluble chromates in paint aerosol. *Am Ind Hyg Assoc J* 1987; 48:830–7.

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