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The efficiency of alkaline extraction for the recovery of hexavalent chromium (Cr^{VI}) from paint samples and the effect of sample storage on Cr^{VI} recovery

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Workplace exposures to Cr^{VI}, a human carcinogen, are significant in spraying operations of chromate-containing paints. Accurate determination of Cr^{VI} in paint aerosol air samples is important in assessing a worker's exposure to Cr^{VI}. National Institute for Occupational Safety and Health method 7604 is widely used for determining Cr^{VI} in air samples. It utilizes an alkaline extraction procedure. It was historically validated for paint aerosol samples containing 24.5 to 61.5 μg of Cr^{VI}. The literature documented potential airborne Cr^{VI} exposures greater than 61.5 μg in recent paint spraying operations. The efficiency of the alkaline method at extracting Cr^{VI} from paint samples containing 250 to 3000 μg of Cr^{VI} was determined. Paint was prepared, sampled, extracted twice and then digested. Extracts were analyzed for Cr^{VI} and digestates of the residual Cr were analyzed for total Cr. Alkaline extraction of paint samples using NIOSH method 7604 resulted in quantitative recoveries for paint samples with Cr^{VI} filter loadings from 250 to 3000 μg. A decrease in Cr^{VI} extraction efficiency was observed in samples containing >1000 μg of Cr^{VI}. A second extraction improved the recovery of Cr^{VI} in these samples. Refrigerating paint aerosol samples for up to 2 weeks did not affect their Cr^{VI} content.

Introduction

Chromium (Cr) is a ubiquitous element in the environment and can exist in various chemical valence states ranging from Cr^{-II} to Cr^{VI}. The more stable chemical forms, trivalent chromium (Cr^{III}) and hexavalent chromium (Cr^{VI}), are the most prominent in the environment.[1] The chemical state of chromium influences the health effects from inhalation exposure to chromium. Cr^{III} has limited toxicity, while Cr^{VI} poses a significant risk of cancer and other health effects to the respiratory system including the nasal passages. Cr^{VI} has been classified by the International Agency for Research on Cancer (IARC) as a Group 1 human carcinogen[2] and by the US Environmental Protection Agency (EPA) as a Group A inhalation carcinogen.[3]

Cr^{VI} is found in chromate-based paints. Chromate-based paint primers are applied, as a first-coat primer, for corrosion inhibition. These paint primers generally consist of a paint matrix containing a sparingly soluble chromate salt such as strontium chromate. The chromate-based paints contain an epoxy primer, a chromate salt, a combination of organic solvents, dispersion agents and other fillers. Spray painting of chromate-containing paint represents an important source of potential occupational exposure to Cr^{VI}. A variety of industries utilize chromate-containing paint, including the aerospace industry. The chromate-based paint primers are generally sprayed on to metal parts and paint sprayers are potentially exposed through inhalation of Cr^{VI}.

In order to study worker exposure to spray paint, air samples have to be collected and analyzed for Cr^{VI}. The determination of Cr^{VI} in air samples has been shown to present problems which may lead to underestimation of the airborne concentration of Cr^{VI}.[4] The problem of underestimation of Cr^{VI} is due to the instability of Cr^{VI} in certain environments resulting in reduction to Cr^{III}. Organic compounds and acidic media have been shown to cause Cr^{VI} reduction to Cr^{III}.[1,4–6]

A number of methods have been developed for Cr^{VI} determination. These methods include a separation technique to separate the Cr^{VI} species from other Cr valence states followed by a detection technique. In one method, National Institute of Occupational Safety and Health (NIOSH) method 7600,[7] Cr^{VI} is stabilized and extracted in a basic solution of sodium hydroxide and sodium bicarbonate. Cr^{VI} is then separated from other Cr species by selective reaction with 1,5-diphenylcarbazide under acidic conditions and the concentration of the colored complex diphenylcarbazone is determined. This method is suitable for soluble and insoluble chromates but involves acidification of the sample during color development, which may cause losses of Cr^{VI} due to the reduction of Cr^{VI} to Cr^{III}.[8]

Other methods for determining Cr^{VI} utilize ion chromatography for Cr^{VI} separation, and spectrophotometric detection of Cr^{VI}. Such methods include EPA method 3060A[9] for the analysis of soils, sludges and sediments and California Air Resources Board (CARB) method 425[10] for the analysis of stationary source emissions. Neither of these methods has been validated for the determination of Cr^{VI} in paint samples.

Another NIOSH published method, 7604,[11] has been applied to the determination of insoluble chromates in paint aerosol. The method was developed and evaluated by Molina and Abell.[12] It utilizes an alkaline solution containing 2% NaOH and 3% Na_2CO_3 for sample preparation, and ion chromatography followed by complex formation with diphenyl carbazide and subsequent column conductivity detection of the Cr^{VI} complex. The evaluation of NIOSH method 7604 was limited to paint aerosol samples containing 24.5 to 61.5 μg of Cr^{VI} per sample. The Occupational Safety and Health Administration recently developed an analytical method, OSHA method ID-215,[13] for the determination of Cr^{VI} in workplace air samples. The method utilizes an alkaline/buffer solution of 10% Na_2CO_3/ 2% $NaHCO_3$/phosphate buffer/ magnesium sulfate to extract

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samples. OSHA method ID-215 was found acceptable for the recovery of Cr^{VI} in spray paint samples with soluble-Cr^{VI} filter loadings of 0.4 to 32 μg.[14]

More recently, a method was developed by Wang and coworkers[15] for the determination of Cr^{VI} in the field by ultrasonic extraction in an alkaline solution of $(NH_4)_2SO_4$ and NH_3 followed by solid-phase extraction of Cr^{VI}. The utility of this method for the speciation of Cr^{VI} in field samples was evaluated by Wang and coworkers[16] using certified welding dust samples with known reference Cr^{VI} concentration; average recovery values of 99% were reported on samples with Cr^{VI} filter loadings of 3 to 34 μg. The same group[14] found this method acceptable for the recovery of Cr^{VI} from spray paint samples with Cr^{VI} mass loadings of 0.4 to 32 μg; recoveries were $>75\%$.

The study reported here was conducted with the following objectives: (1) to determine the extraction efficiency of NIOSH method 7604 for the recovery of Cr^{VI} from paint samples with Cr^{VI} filter loadings ranging from 250 to 3000 μg and (2) to assess the effect of sample storage time on the valence stability of Cr^{VI} in paint aerosol samples with Cr^{VI} filter loadings averaging 1070 μg.

Experimental

Equipment

Ion chromatography/ spectrometry. Cr^{VI} was separated from other Cr species with a Dionex IonPac AG7 analytical column equipped with a Dionex AS40 autosampler and Dionex NG1 guard column (Dionex, Sunnyvale, CA, USA). The colored Cr^{VI}–diphenyl carbazide complex from the post-column reaction was analyzed with a Shimadzu SPD-10Ai UV–visible detector (Shimadzu Scientific Instruments, Inc., Columbia, MD, USA).

Inductively coupled plasma atomic emission spectrometry (ICP-AES). A Leeman Plasma Spec I ICP (Leeman Labs Inc., Lowell, MA, USA) was used for total Cr determination.

Reagents

The paint product used for sample generation in the experiments was water reducible epoxy primer product 44-GN-11 (Deft Incorporated, Irvine, CA, USA), a product widely used by the aerospace industry for priming commercial and military airplanes. Reagent grade $SrCrO_4$ powder of 99.99% purity (GFS Chemicals Incorporated, Columbus, OH, USA) was used for spiking studies. The water used in making paint consisted of Milli-Q ultrapure water of 18 MΩ resistivity (Millipore Corporation, Bedford, MA, USA).

Reagents used for sample preparation and extraction were as specified in the standard analytical method NIOSH 7604.[11]

Reagents used to prepare samples for total Cr determination were as prescribed by CARB method 425.[10] Reagents were selected based on EPA SW 846[17] for total Cr sample analysis.

The solvent, 1,4-dioxane (CAS 123-91-1), used for second Cr^{VI} extractions and total Cr digestions was of analytical-reagent grade (Fisher Chemical, Pittsburgh, PA, USA).

Nitric acid solutions used for glassware cleaning were prepared using trace metal grade HNO_3 (Fisher Chemical, Pittsburgh, PA, USA) diluted in Milli-Q ultra pure water (US Filter, Lowell, MA, USA).

Experimental procedures

Extraction efficiency of NIOSH method 7604. Paint was mixed in the laboratory and aliquots of the paint were sampled. Samples were prepared and analyzed for Cr^{VI} and total Cr in order to study the recovery efficiency of alkaline extraction from paint samples containing 250 to 3000 μg of Cr^{VI} per sample.

Paint preparation. The paint product used to generate samples in this recovery study was made of three components: a polyamide resin base component, an epoxy resin catalyst converter and water. This paint product supplied to the industry contained strontium chromate ($SrCrO_4$) at 10.6% by weight after paint mixing. The manufacturer provided our study with the paint product free of $SrCrO_4$. The paint base was then spiked with $SrCrO_4$ powder to achieve the required proportion of $SrCrO_4$ by weight (10.6%). The base component and the $SrCrO_4$ were placed in a 500 ml acid-washed Wheaton bottle and mixed in a rotating shaker. The shaker rotated at a speed of about 1300 rpm in a temperature-controlled environment of 24–27 °C. The paint catalyst and water were then added to the chromate-containing base component and mixed in the shaker. The ratio of base to catalyst recommended by the manufacturer was 2 : 1. Water in the paint served as a suspending medium and allowed paint application *via* spraying. A systematic mixing procedure was followed throughout the experiment to ensure homogeneity of paint solutions. The paint mixing ratios, the total volume of paint solution made, the paint aliquot volume and the resulting mass of Cr^{VI} deposited on the filters are shown in Table 1.

Paint sampling. A calibrated Rainin air displacement Pipetman P100 adjustable to 1.0 μl (Fisher Scientific, Pittsburgh, PA, USA) or a 25 μl P.C.R. positive displacement pipet adjustable to 0.1 μl (Tri-Continent Scientific, Grass Valley, CA, USA) was used for sampling paint. The P.C.R. pipet was used for sampling 20 μl aliquots of paint. The Rainin pipet was used for sampling 40 and 75 μl aliquots. Paint samples were deposited onto six 35 mm, 0.5 μm pore size, Gelmann PVC filters. The filters were pre-weighed on a Cahn 25 automatic electrobalance (Orion Research Inc., Boston, MA, USA) to the nearest 0.01 mg. Three of the beakers containing filters were labeled as wet paint samples and filters were placed into the Cr^{VI} extraction solution wet-paint-side down. The other three paint filter samples were allowed to dry in a dessiccator at room temperature. The dessiccator was purged with nitrogen gas every time it was opened to avoid any oxidation of lower valence states of Cr to Cr^{VI}. Paint was considered dry on a filter when the filter weight remained stable, within a 5% error margin, over three consecutive weighings. Filters were weighed every hour using the Cahn 25 automatic electrobalance. The filters were dry after about 3 h.

Sample preparation and Cr^{VI} determination. Samples were prepared and analyzed for Cr^{VI} as shown in Fig. 1. Samples were prepared by the standard alkaline extraction method of NIOSH method 7604.[11] Samples were then extracted a second time, using the alkaline extraction of NIOSH method 7604, to recover any residual Cr^{VI}. The second extraction included one

Table 1 Extraction efficiency study: experimental procedures

Paint mixing ratio by volume of base : catalyst : water	Paint solution volume/ml	Paint aliquot volume/μl	Cr^{VI}loading/ μg
Recovery study:			
2 : 1 : 15	180	20	250
2 : 1 : 4	71	20	630
2 : 1 : 6	177	40	1000
2 : 1 : 5	167	75	2000
2 : 1 : 3	168	40	3000
Effect of sample storage			
2 : 1 : 4	186	—	—

modification: 2 ml of the solvent, 1,4-dioxane, were added to the samples before starting the second extraction in order to enhance the extraction process of Cr from the paint matrix. 1,4-Dioxane was selected because it is a polar organic solvent capable of dissolving the organic paint matrix. Empirical observation indicated that 1,4-dioxane broke up the paint samples into strands and filaments. This increased the surface area of the paint available to the extraction solution and enhanced the extraction of Cr from the paint matrix.

CARB method 425[10] was used to analyze the extracts for $\mathrm{Cr^{VI}}$ by ion chromatography and spectrophotometry.

Two filter blanks, two reagent blanks and three blank spikes were processed with each set of paint samples. A blank spike consisted of a solution with known amounts of $\mathrm{Cr^{VI}}$ added to a blank filter. A set of paint samples consisted of three dry and three wet paint samples. Method quality control measures are described in Table 2. All glassware and bottles used were soaked in 1 + 1 $\mathrm{HNO_3}$ overnight and triple-rinsed with Milli-Q ultra pure water before use.

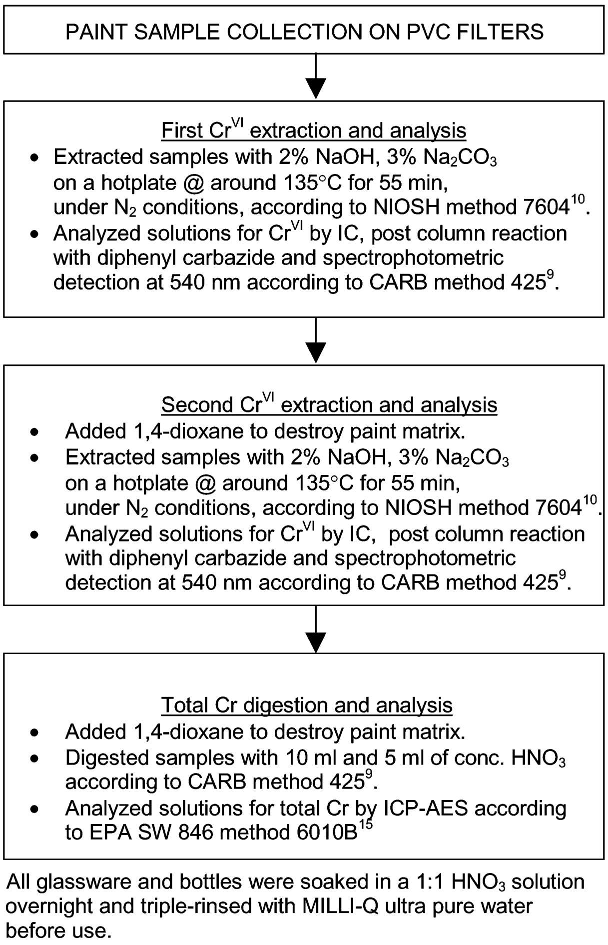

Fig. 1 Paint sample preparation and analysis methods.

Sample preparation and total Cr determination. CARB method 425[10] was used to prepare samples for the determination of residual total Cr on filters (Fig. 1). One modification introduced to the Cr digestion method was the addition of 2 ml of 1,4-dioxane prior to acid digestion, using a 2 ml volumetric pipet, to each sample in order to enhance the digestion process. After the addition of 1,4-dioxane, each beaker was covered with a watchglass for 30 min inside a chemical fume-hood. Beakers were then uncovered and the solvent was allowed to evaporate completely. Samples, blanks and blank spikes were then acid digested. A blank spike consisted of a solution with known amounts of $\mathrm{Cr^{VI}}$ added to a blank filter.

Digested samples were analyzed for Cr by ICP-AES according to EPA SW 846 analytical method 6010B,[17] a method used for determining Cr in complex matrices such as soil, industrial and organic wastes, sludges and sediments (Fig. 1). Measures taken to ensure the quality of Cr measurements are described in Table 2.

Effect of paint sample storage on $\mathrm{Cr^{VI}}$ recovery. This experiment sought to evaluate the effect of sample storage on $\mathrm{Cr^{VI}}$ recovery in samples of paint aerosol. Paint was prepared in the laboratory as described previously. Paint aerosol samples were generated and stored for different time periods. Samples were then analyzed for their $\mathrm{Cr^{VI}}$ and total Cr contents.

Paint preparation. Paint was mixed in the ratio described in Table 1 then transferred into the fluid pressure cup of a spray gun in the study of $\mathrm{Cr^{VI}}$ stability in paint aerosol samples.

Paint aerosol generation. Paint aerosol was generated by a spray gun to study the effect of sample storage on $\mathrm{Cr^{VI}}$ recovery. The gun consisted of a 1 quart Mach 1 Model 98–1130 high-volume, low-pressure (HVLP) gun (Binks Manufacturing , Franklin Park, IL, USA) connected to a 1 horsepower portable air compressor Model 3Z406G (Campbell Hausfeld, Harrison, OH, USA). An oil and water extractor, Binks Model 96-945 (Binks Manufacturing), was placed in-line between the spray gun and the air compressor to supply water-free and oil-free air to the gun. The extractor was outfitted with a Binks Model 85-225 regulator (Binks Manufacturing) to control the air pressure of the spray gun. The regulator was set at about 80 psi.

Paint sampling. PVC Gelmann filters (37 mm, 5.0 μm pore size) were placed in 20 open-face 37 mm filter cassettes for

Table 2 Average recovery results (standard deviation) for quality control (QC) samples

	QC of sample preparation methods			QC of sample analysis methods		
$\mathrm{Cr^{VI}}$ filter loading/μg	Total no. of QC samples[a]	Average $\mathrm{Cr^{VI}}$ recovery (%) Blank spike[b]	Average total Cr recovery (%) Blank spike[b]	Total no. of QC samples[c]	Average $\mathrm{Cr^{VI}}$ recovery (%) Spike[d]	Average total Cr recovery (%) Spike[d]
250	14	98.4 (0.6)	94.1 (1.8)	13	100 (1.5)	100 (1.5)
630	14	96.3 (1.5)	95.5 (0.4)	13	100 (1.5)	100 (1.5)
1000	14	101 (1)	105 (1)	13	96.0 (2.4)	92.4 (1.6)
2000	14	99.3 (1.2)	100 (1)	13	96.0 (2.4)	92.4 (1.6)
3000	14	96.7 (0.8)	94.2 (8.5)	22	101 (1.4)	108 (0.6)

[a] QC samples included reagent blanks, blank filters (filter and de-ionized water) and blank spikes. [b] Blank spike (spiking solution was added to a blank filter): spiking levels ranged from 100 to 3000 μg of $\mathrm{Cr^{VI}}$. [c] QC samples included instrument calibration check samples, duplicates, blanks (de-ionized water) and spikes. [d] Spike: spiking levels ranged from 31.7 to 240 μg of $\mathrm{Cr^{VI}}$.

sampling paint . The experimental set- up is illustrated in Fig. 2. A metal stand was placed inside a 0.6 × 0.8 m wooden box. Three filter holders were placed on the horizontally placed metal stand. The filter cassettes were placed 16.5 cm apart on the horizontal stand. A fourth filter cassette was placed outside the box and served as blank. The filters were then sprayed with the chromate paint for about 30 s or until a visible paint film was deposited on their exposed surface. Five sets of paint aerosol samples were generated. Each sample set consisted of three samples and one blank.

Sample preparation and analysis. The filters on to which paint was sprayed were removed from the filter cassettes and placed, paint-side-down, in an alkaline Cr^{VI}-stabilizing extraction solution (2% NaOH, 3% Na_2CO_3). The first set of samples was removed from the filter cassettes and placed in the alkaline solution within 18 s after sampling. The second, third, fourth and fifth sets of paint samples were removed from the cassettes, transferred to acid-washed Petri dishes, sealed with Parafilm and aged in a refrigerator for 24 h, 48 h, 1 week and 2 weeks. At the end of each aging period, the filters containing the paint samples were placed in the alkaline extraction solution and analyzed for Cr^{VI} and total Cr. Two blank spikes and a blank were processed with each set of three paint aerosol samples.

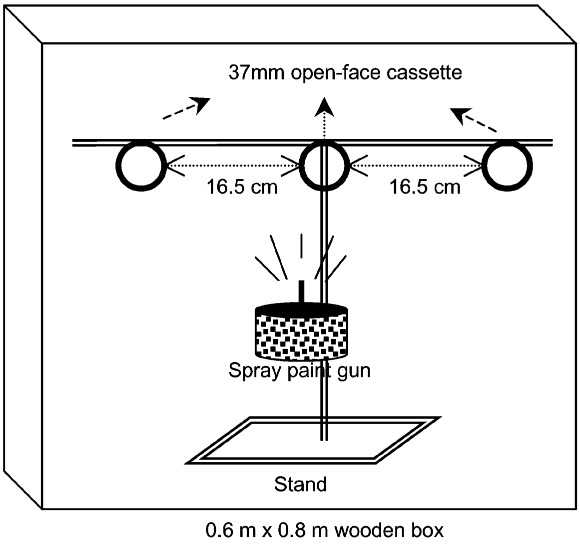

Fig. 2 Effect of paint sample storage on Cr^{VI} recovery: experimental set-up.

Data analysis. In the study of the extraction efficiency of NIOSH method 7604, percentage recoveries of Cr^{VI} relative to expected Cr were calculated for each paint sample. Expected values of Cr mass were based on gravimetric determination of the paint mass deposited on each filter sample and the composition of the paint mixture. A one-way analysis of variance test (ANOVA) was conducted to determine the effect of Cr^{VI} filter loading on method recovery efficiency. Tukey's Studentized Range (HSD) test was used to adjust for multiple comparisons. Two-way factorial ANOVAs were run for each Cr^{VI} extraction and for total Cr digestion in order to compare Cr^{VI} recovery rates between dry and wet samples while simultaneously accounting for differences in the Cr^{VI} filter loadings.

The ratios of recovered Cr^{VI} to total Cr mass obtained for paint aerosol samples stored for different time periods were averaged for each storage-time period and compared in the study of the effect of sample storage on Cr^{VI} recovery in paint aerosol samples. An unpaired *t*-test was used to compare the average Cr^{VI}/total Cr ratio between paint aerosol samples stored for 18 s and those stored for 2 weeks, and between samples stored for 18 s and those stored for 24 h.

Results

Extraction efficiency of NIOSH method 7604

This study sought to determine the efficiency of an alkaline solution in extracting Cr^{VI} from a paint matrix with Cr^{VI} filter loadings ranging from 250 to 3000 μg. Thirty samples were collected, of which 14 were processed while the paint was wet and 16 were processed when the paint was dry. Wet paint samples consisted of paint aliquots deposited on filters, which were immediately placed in a Cr^{VI}-stabilizing extraction solution. Dry paint samples were samples in which the paint was allowed to dry in a nitrogen-purged desiccator, for about 3 h, before the samples were placed in the Cr^{VI}-stabilizing alkaline extraction solution.

The mean percentage recoveries of Cr^{VI} from dry paint samples at various Cr^{VI} loadings are presented in Table 3. Extracting dry paint samples once and analyzing them for Cr^{VI} resulted in an overall Cr^{VI} recovery (all loading levels included), of 90.8 ± 4.4%. A second extraction resulted in an additional average Cr^{VI} recovery of 4.7% ± 4.2%, yielding a total average Cr^{VI} recovery of 95.5 ± 4.5%. A final total Cr digestion resulted in an average overall Cr recovery of 96.6 ± 4.5%. A decrease in the efficiency of the first Cr^{VI} extraction was observed with Cr^{VI} filter loadings >1000 μg. The

Table 3 Extraction efficiency study: effect of filter loading on Cr percentage recovery

	Cr^{VI} filter loading							
	All samples (mean ± *s*)	250 μg (mean ± *s*)	630 μg (mean ± *s*)	1000 μg (mean ± *s*)	2000 μg (mean ± *s*)	3000 μg (mean ± *s*)	*F*-statistic (d.f.) value	*p*-value
Dry paint:	$n = 16$	$n = 3$	$n = 4$	$n = 3$	$n = 3$	$n = 3$		
1st extraction	90.8 ± 4.4	91.1 ± 2.4	93.1 ± 3.6	93.2 ± 4.3	89.7 ± 2.0	86.3 ± 6.9	(4,11) 1.49	0.27
2nd extraction	4.7 ± 4.2	0.4 ± 0.1	8.7 ± 4.2	1.7 ± 0.7	3.5 ± 1.3	7.6 ± 4.2	(4,11) 5.26	0.013
1st + 2nd extractions	95.5 ± 4.5	91.5 ± 2.5	101.8 ± 0.8[a]	94.9 ± 4.0	93.2 ± 1.5	93.9 ± 3.0	(4,11) 9.35	0.002
Total Cr recovery[c]	96.6 ± 4.5	92.6 ± 2.4	103.1 ± 0.6[a]	95.8 ± 3.9	94.0 ± 1.7	95.3 ± 2.7	(4,11) 10.64	<0.001
Wet paint:	$n = 14$	$n = 2$	$n = 3$	$n = 3$	$n = 3$	$n = 3$		
1st extraction	94.8 ± 4.1	94.8 ± 0.7	98.1 ± 1.2[b]	98.0 ± 0.6[b]	93.9 ± 5.0	89.3 ± 2.1[b]	(4,9) 5.57	0.016
2nd extraction	1.4 ± 2.7	0.1 ± 0.0	0.1 ± 0.0	0.1 ± 0.1	0.7 ± 0.3	5.4 ± 4.1	(4,9) 4.04	0.038
1st + 2nd extractions	96.2 ± 3.0	94.9 ± 0.8	98.2 ± 1.2	98.1 ± 0.7	94.6 ± 5.3	94.7 ± 2.6	(4,9) 1.28	0.35
Total Cr recovery[c]	97.2 ± 2.7	96.9 ± 0.6	98.8 ± 1.1	98.5 ± 0.6	95.5 ± 5.3	96.0 ± 2.6	(4,9) 0.79	0.56

[a] Paint samples with a Cr^{VI} filter loading of 630 μg had significantly more Cr^{VI} recovered after the 1st + 2nd extractions and after the total Cr digestion than all other filter loading levels (Tukey's HSD test, $p < 0.05$). [b] Paint samples with a Cr^{VI} filter loading of 3000 μg had significantly less Cr^{VI} recovered in the 1st extraction than paint samples with filter loadings of 630 and 1000 μg (Tukey'sHSD test, $p < 0.05$). [c] Total Cr recovery (%) = Cr^{VI} recovery from 1st extraction (%) + Cr^{VI} recovery from 2nd extraction (%) + residual Cr recovery from digestion (%).

differences in the mean percentage recoveries between the various Cr$^{\mathrm{VI}}$ loadings of the first extraction were not statistically significant (p = 0.27) (Table 3). A decrease in the efficiency of the second extraction was observed for Cr$^{\mathrm{VI}}$ filter loadings >1000 μg. The difference in the mean percentage recoveries between the various Cr$^{\mathrm{VI}}$ loadings of the second extraction were statistically significant (p = 0.013). Paint samples with a Cr$^{\mathrm{VI}}$ filter loading of 630 μg had significantly more Cr$^{\mathrm{VI}}$ recovered at the second extraction than those at the 250 μg loading (Tukey's HSD test, $p < 0.05$).

The recovery data for Cr$^{\mathrm{VI}}$ in wet paint samples are given in Table 3. The overall mean recovery in the first Cr$^{\mathrm{VI}}$ extraction of wet samples was 94.8 ± 4.1%. A second extraction resulted in additional average Cr$^{\mathrm{VI}}$recovery of 1.4 ± 2.7%. A final total Cr digestion of the paint samples resulted in a mean overall Cr recovery of 97.2 ± 2.7%. A decrease was observed in the efficiency of the first Cr$^{\mathrm{VI}}$ extraction at Cr$^{\mathrm{VI}}$ filter loadings of 2000 and 3000 μg . The differences in the mean percentage recoveries between the various Cr$^{\mathrm{VI}}$loadings of the first and second extractions examined separately were statistically significant (p = 0.016) (Table 3). Paint samples with filter loadings of 3000 μg had significantly less Cr$^{\mathrm{VI}}$ recovered in the first extraction than those at the filter loadings of 630 and 1000 μg (Tukey's HSD test, $p < 0.05$).

The data in Table 3 show that the improvements in Cr$^{\mathrm{VI}}$ recovery provided by the second Cr$^{\mathrm{VI}}$ extraction were higher for dry paint than wet paint samples at each Cr$^{\mathrm{VI}}$ filter loading level.

The Cr$^{\mathrm{VI}}$ and total Cr recovery rates between dry and wet samples were compared while accounting for differences in the loadings. There was a significant effect based on whether the paint was dry or wet for both the first [F-statistic = 9.75 with (1,20) degrees of freedom and p = 0.006] and second extractions [F-statistic = 11.25 with (1,20) degrees of freedom and p = 0.003]. There was a significant difference between the recoveries of wet and dry paint samples from the first extraction, in 12 out of 30 samples and at filter loadings of 250, 1000, 2000 and 3000 μg. The recovery of Cr$^{\mathrm{VI}}$ was lower in dry paint samples for the first Cr$^{\mathrm{VI}}$ extraction and the total Cr digestion procedures. Whether the paint was wet or dry did not affect the overall recovery of Cr after a sample was subjected to two Cr$^{\mathrm{VI}}$ extractions and a total Cr digestion (F-statistic = 1.06 with (1,20) degrees of freedom and p = 0.32] while taking into account all the different Cr loading levels.

Effect of paint sample storage on Cr$^{\mathrm{VI}}$ recovery

Fourteen samples, stored for different time periods in a refrigerator, were analyzed for Cr$^{\mathrm{VI}}$ and total Cr in order to determine the effect of sample storage on Cr$^{\mathrm{VI}}$ recovery in paint aerosol samples. Table 4 shows the ratio of Cr$^{\mathrm{VI}}$ mass recovered from two extractions to total Cr mass recovered in the samples. The mass of all Cr measured from the filters ranged from 726 to 1190 μg. There was a statistically significant difference between the average Cr$^{\mathrm{VI}}$: total Cr ratio obtained from paint aerosol samples stored for 18 s and samples stored for 2 weeks (t-statistic = 8.62 with 3 degrees of freedom and p = 0.003). There was no statistically significant difference between the average Cr$^{\mathrm{VI}}$: total Cr ratio obtained from paint aerosol samples stored for 24 h and samples stored for 2 weeks (t-statistic = −0.85 with 3 degrees of freedom and p = 0.457).

Table 4 Effect of paint sample storage on Cr$^{\mathrm{VI}}$ recovery

Sample storage time	Cr mass filter loading/μg	Cr$^{\mathrm{VI}}$ mass : total Cr mass	
18 s	1170	0.998	0.998 ± 0.000[a]
	1460	0.998	
	1420	0.998	
24 h	979	0.061	0.970 ± 0.008[a]
	1190	0.973	
	1190	0.976	
48 h	726	0.988	0.988 ± 0.001[a]
	775	0.988	
	793	0.989	
1 week	1040	0.963	0.982 ± 0.016[a]
	1260	0.991	
	1490	0.991	
2 weeks	747	0.972	0.975 ± 0.005[a]
	780	0.979	

[a] Average ± s.

Discussion

Extraction efficiency of NIOSH method 7604

This study aimed at determining the efficiency of a widely used alkaline extraction procedure for extracting Cr$^{\mathrm{VI}}$ from paint samples with Cr$^{\mathrm{VI}}$ mass filter loadings similar to what would be obtained in sampling paint spraying operations of industrial facilities. The efficiency of this extraction procedure published in NIOSH method 7604[11] was previously determined for paint samples containing only 24.5–61.5 μg of Cr$^{\mathrm{VI}}$ by Molina and Abell.[12]

Actual Cr$^{\mathrm{VI}}$filter mass loadings in samples collected in industrial settings may be greater than 61.5 μg. A study of aircraft paint spraying operations by Zhuang and Myers[18] reported exposure concentrations to chromium during paint primer spraying ranging from 0.4 to 4283.3 μg m^{-3}. The average male worker inhales about 10 m^{3} of air per 8 h work shift,[19] meaning that some workers in the study by Zhuang and Myers[18] were potentially exposed to 42830 μg of chromium during an 8 h workshift. Workers in military aircraft priming operations were exposed to airborne Cr$^{\mathrm{VI}}$ concentrations ranging from 101 to 403 μg m^{-3} in a study by Wang and coworkers.[16] These workers were potentially exposed to 1000–4000 μg of Cr$^{\mathrm{VI}}$ in an 8 h workshift. A worker spraying chromate-containing paint and exposed to Cr$^{\mathrm{VI}}$ levels at the current OSHA PEL of 0.1 mg m^{-3} could be exposed to 1000 μg of Cr$^{\mathrm{VI}}$ in an 8 h work shift.

In this study, the extraction efficiency of the alkaline method described in the ion chromatography method, NIOSH method 7604, for the extraction of Cr$^{\mathrm{VI}}$ from paint samples was determined for paint samples with Cr$^{\mathrm{VI}}$filter loadings ranging from 250 to 3000 μg. The recovery of Cr$^{\mathrm{VI}}$ from the first extraction ranged from 80.6 to 104%. A decreasing trend in the efficiency of alkaline extraction was observed for paint samples with Cr$^{\mathrm{VI}}$ filter loadings >1000 μg. A second extraction improved the recovery of Cr$^{\mathrm{VI}}$ in these samples. This observed decrease in Cr$^{\mathrm{VI}}$ recovery may be attributed to the resistant properties of industrial paint matrices reported by others.[12,13,20] The extraction method for the recovery of Cr$^{\mathrm{VI}}$ from paint samples met NIOSH[21] and OSHA[13] criteria for method accuracy. The minimum recovery recommended by NIOSH and OSHA for acceptable quantitative recovery is 75%.

1,4-Dioxane was introduced to the paint samples prior to performing the second Cr$^{\mathrm{VI}}$ extraction in this investigation. The effect of 1,4-dioxane on the improvement in Cr$^{\mathrm{VI}}$ alkaline extraction efficiency was not determined. However, 1,4-dioxane was selected because it is a polar organic solvent that could dissolve the organic paint matrix. Empirical observation indicated that 1,4-dioxane broke up the paint samples into smaller strands and filaments. This increased the surface area of the paint exposed to the extraction solution and could have enhanced the extraction of Cr from the paint matrix. 1,4-Dioxane was added to paint samples only prior to the second Cr$^{\mathrm{VI}}$ extraction procedure and the final Cr digestion step. It did not affect the quantitative recoveries of the first extraction procedure.

Cr^{VI} extraction efficiency using NIOSH method 7604 decreased as the Cr^{VI} content in paint samples increased above 1000 μg. The decrease in Cr^{VI} recovery was not due to reduction of Cr^{VI} to other valence states since a second Cr^{VI} extraction improved the mean Cr^{VI}recovery values of dry paint samples by 3.5 and 7.6% and wet paint samples by 0.7 and 5.4% in samples with Cr^{VI}loadings of 2000 and 3000 μg, respectively.

The final total Cr analysis of paint samples resulted in a slight increase in Cr recovery. This improvement in mean Cr recovery ranged only from 0.4 to 2.0%. Nonetheless, this indicates that not all of the sampled Cr was in the Cr^{VI} form; some Cr^{III} or metallic Cr, Cr^0, must have been present. Cr^{VI} reduction to Cr^{III} may have occurred during sampling owing to matrix effects or the presence of reducing agents such as organics, acid constituents and iron.[1,4–6,22] Reduction of Cr^{VI} to Cr^{III} has been reported on sampling filter media such as cellulose ester filters.[6,13,23,24] However, cellulose ester and polytetrafluoroethylene filter media appear to not be a problem if samples are prepared quickly.[25] Cr^{VI} reduction is unlikely to have occurred on the PVC filters used in this study.[11–13] Treating filters with base prior to use is recommended if Cr^{VI} reduction during sampling is anticipated.[26]

Oxidation of Cr^{III} to Cr^{VI}has been reported during analysis of workplace air samples containing Cr^{III}.[27,28] Although the only source of Cr in the paint used in this study was hexavalent, there is a potential for Cr^{III} to be present owing to reduction of Cr^{VI}. Our data showed that only 0.4–2% of the Cr recovered from the paint samples was in a valence state other than Cr^{VI}. Therefore, Cr^{III} oxidation or Cr^{VI}reduction is not likely to have occurred significantly. The addition of a precipitation agent (magnesium sulfate) to the alkaline extraction solution can minimize potential Cr^{VI} positive bias due to air oxidation of Cr^{III} to Cr^{VI} during preparation of paint samples potentially containing Cr^{III}, as described in OSHA method ID-215.[13] Analyzing workplace air samples containing different Cr species can be challenging and is often a concern in many workplace situations because matrix components can influence the interconversion between Cr^{VI} and Cr^{III}.[29,30] Oxidation of Cr^{III} and reduction of Cr^{VI}were reported in soil samples containing organics, iron and manganese compounds.[29] The use of an alkaline ammonium buffer solution was shown to minimize Cr^{VI}reduction and Cr^{III} oxidation during preparation of such samples.[16,31–33]

Effect of paint sample storage on Cr^{VI} recovery

The effect of sample storage on Cr^{VI} recovery in paint samples on filters stored for different time periods prior to analysis was assessed. Storing paint aerosol samples with a an average Cr^{VI} mass filter loading of 1055 mg, in a refrigerator, for 24 h, 48 h, 1 week and 2 weeks did not affect the amount of Cr^{VI} recovered from the samples. The mean recovery of Cr^{VI} relative to total Cr in samples stored for 2 weeks was statistically significant from the mean recovery of samples stored for only 18 s. However, the difference between the two mean recoveries was only 2.3%, which is insignificant as a practical matter. There was no statistically significant difference between the mean recovery of Cr^{VI} relative to total Cr in samples stored for 24 h and samples stored for 2 weeks. The slight loss of Cr^{VI} observed in stored paint filters appears to be due to the reduction of Cr^{VI} to lower valence states of Cr during the drying of paint samples in the first 24 h. The reduction of Cr^{VI} to lower Cr valence states has been reported by others in aerosol matrices found in the workplace[4] such as welding fumes.[6,24] Overall, our findings support the stability of Cr^{VI} observed by Molina and Abell[12] in paint samples with average Cr^{VI} filter loadings of 28.3 μg, over 2 weeks. Based on the results of this experiment, refrigerating paint aerosol samples for 2 weeks or less is not likely to affect significantly the Cr^{VI} content in the paint samples and the measured airborne concentration of Cr^{VI}.

Conclusion

The results from this study show that extracting PVC filters with an alkaline solution is acceptable for the recovery of Cr^{VI} from paint samples. The method can be used to assess airborne concentrations of occupational exposures to Cr^{VI} during paint priming applications generating up to 3000 μg of Cr^{VI} per sample. Also, reduction of Cr^{VI} does not appear to affect Cr^{VI} measurements when storing paint aerosol samples for up to 2 weeks.

Disclaimer

Mention of company trade names or products does not constitute endorsement by the University of California, Los Angeles or the Research Triangle Institute.

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