Ann. occup. Hyg., Vol. 49, No. 1, pp. 47–59, 2005
© 2004 British Occupational Hygiene Society
Published by Oxford University Press
doi:10.1093/annhyg/meh081

Size Distribution and Speciation of Chromium in Paint Spray Aerosol at an Aerospace Facility

RANIA A. SABTY-DAILY[1], PATRICIA A. HARRIS[2], WILLIAM C. HINDS[2] and JOHN R. FROINES[2]*

[1]Health Science Program, 5151 State University Drive, California State University, Los Angeles, CA 90032-8171, USA; [2]Center for Occupational and Environmental Health, School of Public Health, 650 Charles E. Young Drive South, University of California, Los Angeles, CA 90095-1772, USA

Received 17 July 2001; in final form 30 December 2003; published online 10 December 2004

Spray painters are potentially exposed to aerosol containing Cr(VI) via inhalation of chromate-based paint spray. Two field studies were conducted at an aerospace facility to determine the size distribution and speciation of Cr(VI) in paint spray aerosol. Sampled paint products consisted of sparingly soluble strontium chromate in an epoxy resin matrix, a matrix generally known for its durability and toughness. Personal aerosol samples were collected using Sierra Marple personal cascade impactors and analyzed for Cr(VI) and total Cr. The size distribution of total Cr particles in the paint aerosol had a Mass Median Aerodynamic Diameter (MMAD) of 7.5 μm [Geometric Standard Deviation (GSD = 2.7 μm)] in both field studies. The MMAD of Cr(VI) particles was 8.5 μm (GSD = 2.2 μm). Particles >2 μm constituted 90% or more of the total Cr and the Cr(VI) mass, in all sampled paint aerosols and were lognormally distributed. The target site for respiratory deposition of Cr in the aerosol was estimated based on the mass distribution of Cr according to particle size. On an average, 62% of the Cr and Cr(VI) mass in the paint aerosol consisted of particles >10 μm. This study showed that 71.8% of Cr(VI) mass in paint spray aerosol potentially inhaled by a spray painter may deposit in the head airways region. Only 2.0 and 1.4% of Cr(VI) mass in the paint aerosol may potentially deposit in the alveolar and tracheobronchial region, respectively.

The ratio of Cr(VI) mass to total Cr mass was determined in bulk paint and the data indicate that Cr was predominantly in the Cr(VI) valence state, before spraying. The ratio of Cr(VI) mass to total Cr mass was also determined in paint aerosol samples. The data indicated that there was a reduction of Cr(VI) regardless of Cr aerosol particle size. Cr(VI) reduction occurred most likely during the 8 h sample collection time period. These findings are in agreement with the findings that observed Cr(VI) reduction during collection of airborne Cr(VI) in samples of chromic acid mist. The use of Cr(VI) stabilizing sampling media and the storage of samples at lower temperatures (4°C) during and after sampling may avoid the underestimation of Cr(VI).

Keywords: chromium; hexavalent chromium; paint aerosol; paint spray; particle size; size distribution

---

INTRODUCTION

Chromate-based paints containing Chromium (VI) [Cr(VI)] are applied as a first-coat primer onto metals to protect them from corrosion damage. Paint primers generally contain a chromate salt such as strontium chromate. Historically, there has been widespread use of chromate-containing spray paints as anti-corrosion primers in the aerospace industry. Spray painting of chromate-containing paints represents an important, potential source of occupational exposure to Cr(VI) in this industry.

Cr(VI) poses a significant risk of cancer to the respiratory system (Langard, 1990; Lees, 1991; Gibb *et al.*, 2000). Cr(VI) has been classified as a group 1 carcinogen by the International Agency for Research on Cancer (IARC, 1990) and as a group A carcinogen by the U.S. Environmental Protection Agency (U.S. EPA, 1984). The IARC Working Group on the Evaluation of the Carcinogenic Risk of Chemicals to Humans has summarized the data

---

*Author to whom correspondence should be addressed.
E-mail: jfroines@ucla.edu

on chromium, and concluded that there was sufficient evidence of respiratory cancer in workers involved in chromate production, chromate pigment production and chromium plating (IARC, 1990). IARC has also concluded that the data on lung cancer in other chromium-associated occupations, such as spray painting, and for cancers at sites other than the lung are insufficient.

Studies on the carcinogenic risk of Cr(VI) from spray painting are equivocal. Three epidemiological studies investigated the association between spray painting with chromate primers and lung cancer with differing results. A mortality study of spray painters determined a lung cancer proportionate mortality risk of 1.84 with a positive relationship between lung cancer risk and exposure duration (Dalager *et al.*, 1980). A study of painters in the airplane manufacturing industry found an inverse relationship between lung cancer risk and employment in spray painting (Alexander *et al.*, 1996). A study by Chiazze *et al.* (1980) of automobile spray painters exposed to chromate failed to find an excess of lung cancer risk.

Cases of laryngeal cancer have been reported in paint sprayers (Alexander *et al.*, 1996). Cancer of the nasal cavities and paranasal sinuses were seen in users of chromate paint (Brinton *et al.*, 1984). Cancer of the buccal cavity and pharynx were reported in painters (Chiazze *et al.*, 1980; Dalager *et al.*, 1980). Although suggestive, the studies do not confirm a causal relationship between Cr(VI) exposure during spray painting and cancers of the head airways region.

The particle size distribution of inhaled aerosols has important consequences for deposition in the lung. Penetration of an inhaled particle through the airways generally increases with decreasing particle size for particles >0.5 µm (Gorner and Fabries, 1996). Assessment of the particle size distribution of a paint spray aerosol may be significant to the extent that it provides an understanding of the regional deposition in the lung with implications for the evaluation of potential hazards to workers inhaling the Cr(VI) aerosol within its epoxy matrix. The health effects resulting from inhaled Cr(VI) containing particulate matter may be influenced by the site of deposition within the respiratory system and the overall dosimetry. The size distribution of paint spray aerosol represents an important parameter in estimating the deposition sites of Cr(VI) (Lippmann *et al.*, 1980; ACGIH, 1985).

To study the size distribution of Cr(VI) in paint spray aerosol, 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 that may result in underestimation of the airborne concentration of Cr(VI). Such underestimation may impact the assessment of potential health risks associated with inhaling paint aerosols. Underestimation of Cr(VI) may result from the reduction of Cr(VI) during sample collection, storage and preparation (Gray, 1983; Research Triangle Institute, 1988; Sherwell and Silvers, 1992; Losi *et al.*, 1994). Gray (1983) reported the instability of Cr(VI) in metallic aerosols produced during welding of chromium alloy steels. The Research Triangle Institute (1988) showed that 50% of the Cr(VI) content in chromic acid mist was lost to other chromium valence states in about 16 h, in a laboratory chamber with conditions similar to ambient atmosphere and in field tests. Shin and Paik (2000) found that the percentage ratio of Cr(VI) to total Cr in chromic acid mist was reduced from an initial 100%, immediately after mist generation, to 59%, in an 8 h time period. Other studies have also reported Cr(VI) reduction to Cr(III) in the presence of acids and reducing agents such as organic matter, Fe(0), Fe(II), vanadium and manganese (NIOSH, 1973; Research Triangle Institute, 1988; U.S. EPA, 1991; ATSDR, 1993).

The specific objectives of the study were (i) to assess the size distribution and speciation of Cr in paint spray aerosol in two field studies at an aerospace manufacturing facility, (ii) to evaluate whether reduction of Cr(VI) in paint aerosol samples occurs and whether any reduction is dependent on particle size and (iii) to estimate the fraction of Cr(VI) deposited in the head airways, tracheobronchial and alveolar regions based on Cr aerosol size distributions.

METHODS

Two field studies were conducted to characterize the size distribution and speciation of Cr during the use of chromate-based paints at a aerospace manufacturing facility in Southern California. A preliminary study, Field Study I, evaluated the size distribution of total Cr in paint aerosol generated by priming operations. A second field study, Field Study II, was conducted to assess the size distributions of Cr(VI) and total Cr in paint aerosol, as well as to determine the reduction of Cr(VI) in paint aerosol samples.

Field study I

Description of spray-painting operations. The size distribution of total Cr in the breathing zone of workers conducting chromate-based paint spraying operations was determined in this study. This field study included six separate spray paint booths that were each equipped with a High Volume Low-Pressure (HVLP) mobile hand-held spray gun. Three of the booths, A, B and C, were open face booths with exhaust air baffles, located on their back wall. In two of the open faced booths, A and B, small airplane parts were brought via an automated conveyor system and the workers sprayed these parts such that the spray was directed toward the back of the booth. In the third open-faced booth C, the worker walked into the booth and sprayed the large airplane parts kept on tables. The sprayed paint aerosol was directed toward the sides of the booth as well as the rear of the booth. As a result, the worker was frequently between the spray aerosol and the air baffles. Paint booth D was enclosed and E was open at each end. Large airplane skins (20′ × 10′) were sprayed in booths D and E. An air supply system supplied fresh air from the ceiling in booth D. The downdraft pushed the paint spray down toward a gridded floor under which there was a running stream of water that carried the contaminated air away. Booth E was split into two levels, a top level (E′) and a floor level (E″). Spray painting was done on both levels with two painters working concurrently at each level, painting large airplane skins (20′ × 10′). An air supply system supplied air from the ceiling in booth E. The downdraft sent the air down past the painters in booth E′ and E″, toward a gridded floor under which a running stream of water carried the contaminated air away.

Paint products used were epoxy primers (Table 1). The epoxy primer is a two-component coating consisting of a base and a catalyst. The base reacts with amines and polyamides in the catalyst to form cross-links and chains that provide the coating with its characteristics of toughness and flexibility (Kroschwitz, 1994).

Every worker evaluated in this study used a full-face air-purifying respirator with dual cartridges for removing organic vapors and particulates at the time of sampling. The company had a mandatory respiratory protection program.

Sample collection. Three days of 8 h sampling were conducted. Personal breathing zone air samples of six workers spraying chromate-based paint in six spray booths were collected at the aerospace facility. An eight stage Marple personal cascade impactor (Model 298, Graseby Andersen Samplers, Inc., Atlanta, GA, USA) was connected to a Dupont P-2500 constant flow rate pump (model P-2500, Du Pont Company, Wilmington, DE, USA) to collect personal samples at 2 liters per minute (Lpm). In-line pump calibration was performed with a Mini-Buck calibrator (model M-5, A.P. Buck Inc., Orlando, FL, USA) at the beginning and at the end of each sampling period. The sampling media in the cascade impactors consisted of 5.0 μm pore-size PVC filters (Graseby Andersen Samplers, Inc., Atlanta, GA, USA) in which slots were custom-cut. A field blank consisting of a PVC filter with slots, placed in an open-face 37 mm filter cassette, was collected with each impactor. The cascade impactors were brought to the laboratory and refrigerated inside a dessicator at the end of sampling. Impactors and filter cassettes were then disassembled and filters were

Table 1. Primer products sprayed by paint booth and sampling day

Paint type	Booth/Day	Pigments	Primary solvents	Resin system	Catalyst
DEFT (44GN011)	Field study I: A/1, A/2, C/all, E′/1, E′/3, E″/1, E″/3	Strontium chromate Cobalt phosphate	Sec butyl alcohol	Epoxy resin, polyamide resin	Nitroethane
DESOTO (513X396)	Field study I: B/3	Strontium chromate Titanium dioxide Iron oxide	2-Butoxyethanol 1,1,1-Trichloroethane	Epoxy resin	Aliphatic amine
DESOTO (513X385)	Field study I: B/1, B/3, D/all, E′/2, E″/2	Calcium chromate Titanium dioxide	2-Butoxyethanol 1,1,1-Trichloroethane	Epoxy resin	Aliphatic amine
Deft (44GN060)	Field study II: D/all, E′/all, E″/all	Strontium chromate	Sec butyl alcohol	Epoxy resin, polyamide resin	Nitroethane
Cytec (BR 127)	Field study II: F/all	Strontium chromate	Methyl ethyl ketone Tetrahydrofuran Diacetone alcohol	Epoxy phenolic resin	Formaldehyde

placed in acid-washed plastic petri dishes. Samples were packed with dry ice and sent to a certified commercial laboratory for analysis.

Sample preparation. Filters from each impactor stage including the backup were prepared for Cr analysis according to the National Institute for Occupational Safety and Health (NIOSH) analytical method 7024 (NIOSH, 1994a). Three modifications were introduced to the sample preparation method: (i) PVC filters were used as sampling media instead of mixed-cellulose ester (MCE) filters. Cr(VI) losses due to reduction have been reported on MCE filters (Gray, 1983; Dyg, 1994; Spini, 1994; OSHA, 1998) while minimal Cr(VI) reduction has been reported on PVC filters (Molina and Abell, 1987; NIOSH, 1994b; OSHA, 1998; Shin and Paik, 2000), (ii) ashing of the filters at 400°C in sample preparation was omitted because PVC filters cannot be ashed and (iii) the use of a hotplate during sample preparation was replaced with a microwave.

Sample analysis. Digested samples were analyzed for Cr by Inductively Coupled Plasma-Atomic Emission Spectrometry (ICP-AES) according to EPA SW 846 analytical method 6010B (U.S. EPA, 1996a). A Perkin Elmer Plasma 40 instrument equipped with a Perkin Elmer Autosampler AS90 (Perkin Elmer Instruments, Norwalk, CT, USA) and a UV-vis Detector model CHA-2 (Dionex Corp., Sunnyvale, CA, USA) were used for sample analysis. Samples with total Cr concentrations below the ICP-AES method detection limit of 1 μg/L were analyzed for total Cr by Graphite Furnace Atomic Absorption (GFAA) Spectrometry according to EPA method 218.2 (U.S. EPA, 1983). The GFAA method had a detection limit of 0.004 μg/L. GFAA instruments included a Perkin Elmer Zeeman 5100PC graphite furnace tube equipped with a Perkin Elmer Autosampler AS60 (Perkin Elmer Instruments, Norwalk, CT, USA) and a UV-vis Detector model CHA-2 (Dionex Corp., Sunnyvale, CA, USA). Quality control samples for total Cr analysis included instrument calibration check samples, standard check samples, replicates, blanks and spikes. A blank consisted of deionized water.

Field study II

Description of spray-painting operations. To study the size distribution of Cr(VI) and to determine the valence state of Cr in the different size fractions of primer paint aerosol, a second field study was conducted at the same aerospace facility as in Field Study I. The Cr aerosol in priming operations from four spray booths was evaluated. Two of the booths, D and F were enclosed with a down-draft-water-wash exhaust ventilation system. In these booths large (20′ × 10′) skins of airplane fuselage were sprayed with primer. The three booths D, E′ and E″ were the same as evaluated in Field study I. Table 1 lists the paint products sprayed in the spray booths.

The company had a mandatory respiratory protection program and every worker evaluated in this study used a respirator at the time of sampling. Workers in booths E′, E″ and F wore disposable atmosphere-supplying airline respirators with continuous flow and a hood. The spray painter in booth D wore an air-purifying full-face respirator with dual cartridges for removing organic vapors and particulates.

Sample collection. Paint sprayers in the four spray booths were sampled. Three 8 h personal breathing zone samples from each of the four paint booths were collected on three different days to estimate inter-day variability. The sampling device was an eight-stage Marple personal cascade impactor. Five- micrometer-pore-size PVC filters with custom-cut slots were the sampling media. Three field blanks were collected with each sample. Each field blank consisted of a PVC filter placed on the upper stage of a Marple personal impactor. SKC constant flow rate pumps (model 224-PCXR4, SKC Inc., Eighty Four, PA, USA) were used to collect samples at a flow rate of 2 Lpm. Sampling pumps were calibrated in-line at the beginning and the end of each sampling period using a Mini-Buck calibrator. Collected samples were immediately refrigerated after sampling.

Three 1 ml samples of bulk paint were sampled from each booth on each sampling day using a Rainin Pipetman P100 adjustable to 1.0 μl (Fisher Scientific, Pittsburgh, PA, USA), deposited on a 5.0 μm pore-size PVC filter, placed in a beaker, sealed and refrigerated immediately. The solvents in the Cytec paint product sampled in this field study damaged the filter and so it could not be analyzed for Cr. Remaining bulk Cytec paint samples were collected directly into beakers containing Cr(VI) extraction solutions. A blank filter was processed with each set of three bulk samples.

Sample preparation for Cr(VI) analysis. Cascade impactor filter samples, field blanks, bulk samples and bulk blanks were prepared for Cr(VI) analysis using NIOSH method 7604 (NIOSH, 1994b). The extraction of Cr(VI) during sample preparation was performed for 55 min. One filter blank, one reagent blank and one blank spike were processed with each set of samples for quality control. The blank spike consisted of a solution containing known amounts of Cr(VI) added to a blank filter. Each set of samples consisted of 10 cascade impactor filters, 3 field blanks, 3 bulk samples and a bulk blank. One set of duplicates for every 10 filter samples were sent fot analysis. A sample was split in half to make a pair of duplicate samples. All glassware and bottles used were soaked in a 1:1 HNO_3 solution overnight and rinsed thrice with MILLI-Q ultra pure water before use.

Cr(VI) sample analysis. CARB method 425 (California EPA, 1997) was used to analyze the alkaline extracts for Cr(VI) by ion chromatography and spectrophotometry. An anion exchange separator column, Dionex IonPac AS7 analytical column, equipped with a Dionex NG1 guard column (Dionex Corporation, Sunnyvale, CA, USA) was used to separate Cr(VI) from other Cr species. The colored Cr(VI)-diphenyl carbazide complex was detected by a Dionex UV-visible detector VDM-2 (Dionex Corporation, Sunnyvale, CA, USA) according to EPA method 7196A (U.S. EPA, 1996b). Quality control samples for Cr(VI) analysis included instrument calibration check samples, standard check samples, replicates, blanks and spikes. A blank consisted of deionized water.

Sample preparation for total Cr analysis. CARB method 425 (California EPA, 1997) was used to prepare samples for the analysis of residual Cr on filters by ICP-AES. The total Cr digestion method included one modification: 2 ml of 1,4-dioxane was added to each sample before digestion in order to enhance the digestion process. 1,4-dioxane was selected because it is a polar organic solvent that can dissolve the organic paint matrix. Empirical observation indicated that 1,4-dioxane broke down the paint samples into paint strands and filaments. This increased the surface area of the paint exposed to the extraction solution and enhanced the release of Cr from the paint matrix. After the addition of 1,4-dioxane, each beaker was covered with a watchglass for 30 min inside a chemical fume hood. Beakers were uncovered and the solvent allowed to evaporate completely. Paint aerosol samples and quality control samples were then subjected to acid digestion, following the CARB method 425. One filter blank, one reagent blank and one blank spike were processed with each set of samples for quality control. Solutions with known amounts of Cr(VI) were added to blank filters to make blank spikes. Each set of samples consisted of 10 cascade impactor filters, 3 field blanks, 3 bulk samples and a bulk blank. One set of duplicates for every 10 filter samples were sent for analysis. A sample was split in half to make a pair of duplicate samples.

Total Cr sample analysis. Digested samples were analyzed for Cr as described in Field Study I.

Data analysis

The total Cr and Cr(VI) content of filters from each impactor stage and the backup stage were used to calculate the mass fraction of total Cr and Cr(VI), normalized for interval width in each aerosol sample. This was done in order to describe the way in which Cr is distributed among different particle size ranges. The normalized mass fractions were averaged across all samples. An upper limit of 35 μm was assumed while computing the normalized mass fractions based on a method for defining the upper limit of the first impactor stage (Hinds, 1986). According to this method, the selected upper limit of the first stage can be twice the cutoff size for the first stage (2 × 21 μm = 42 μm) or the cutoff size for the first stage times the ratio of cutoff sizes for the first and second stages (21 μm × 21 μm /15 μm = 29 μm). In this case, the average of the two methods, 35 μm, was used. The cumulative mass fraction of total Cr in aerosol samples of Field Study I was calculated and averaged across different samples. The average cumulative mass fractions of total Cr in samples of Field Study I were plotted on a log probability graph to determine total Cr size distribution. The same procedure was followed for determining the total Cr and Cr(VI) size distribution in aerosol samples of Field study II. The Geometric Standard Deviation (GSD) of a size distribution was estimated only for the lognormally distributed portion of the distribution (particles >2 μm). A GSD was determined by the ratio of particle size associated with a cumulative count of 50% to that associated with a cumulative count of 16%.

The ratio of Cr(VI) mass to total Cr mass was determined for each particle size range of paint aerosol samples collected in Field Study II, in order to estimate the contribution of Cr(VI) relative to total Cr. The ratios were averaged across samples, within each particle size range. The ratio of Cr(VI) to total Cr was also determined in bulk paint samples. The airborne Cr concentration was determined by summing up the Cr content across all the impaction stages. An 8 h Time Weighted Average (TWA) was calculated for each sample.

The percentage fractions of Cr deposited in the head airways, tracheobronchial and alveolar regions of the respiratory tract were estimated for each booth based on a respiratory deposition model developed by the International Commission on Radiological Protection (ICRP, 1994). Deposition fractions were estimated for each size range of each sampled aerosol based on equations developed by Hinds (1999). The midpoint of each of the aerosol size fractions sampled with a cascade impactor was used to estimate deposition fractions for the given size range. The calculated deposition fractions that were estimated and the mass of total Cr and Cr(VI) sampled in each particle size range were used to compute the percentages of total Cr and Cr(VI) mass deposited in the head airways, tracheobronchial and alveolar regions of the respiratory system of an average adult. The percentages were averaged across each spray booth.

The sampling results of booth A on the third sampling day (A/3) and booth B on the second sampling day (B/2) were not included in the result analysis of Field Study I because of accidental sample loss during handling. The sampling results of booth E″ on the second sampling day (E″/2) in Field Study II were not analyzed because many of the total Cr concentrations were below the method detection limit. The ratio of Cr(VI) to total Cr was not calculated for bulk paint samples of booth F on the first and second sampling days of Field Study II because the PVC filters were damaged by the paint and were not available for total Cr analysis.

RESULTS AND DISCUSSION

The first objective of this investigation was to determine the size distribution of Cr and Cr(VI) in aerosols generated by chromate spray paint operations in an aerospace manufacturing facility and to estimate the aerosol fractions deposited in different regions of the respiratory tract. A second objective was to evaluate the reduction of Cr(VI) in paint aerosol samples. The objective of Field Study I was to determine the size distribution of Cr in spray paint aerosol generated by priming operations of an aerospace industry. Field Study II was conducted to assess the size distribution of Cr and Cr(VI) in paint aerosol, as well as to evaluate the reduction of Cr(VI). The paint products in the field studies basically consisted of sparingly soluble strontium chromate in an epoxy resin matrix.

Size distribution of total Cr and Cr(VI)

Table 2 provides the mean and the standard deviation of the percentage of total Cr and Cr(VI) particulate mass in specified size ranges for both field studies. The mass of total Cr and Cr(VI) in paint aerosols consisted primarily of particles >10 µm. Particles >10 µm represented 51.4–66.0% of the total Cr mass in paint aerosol samples of Field Study I, 65.2–73.0% of the total Cr mass in samples of Field Study II and 64.2–70.5% of the Cr(VI) mass in samples of Field Study II.

Cumulative total Cr and Cr(VI) mass fractions were averaged for each particle size range, across paint aerosol samples; the log probability graph of particle diameter by percentage of particles less than a given size is shown in Fig. 1. Particles >2 µm constituted >90% of total Cr mass in all paint aerosols and were lognormally distributed. Similarly, particles >2 µm constituted more than 90% of Cr (VI) mass in paint aerosols and were lognormally distributed. Table 3 provides the Mass Median Aerodynamic Diameter (MMAD) and GSD for the lognormally distributed portion of aerosol size distributions averaged across samples. The MMAD of total Cr particles ranged from 9 to 40 µm in paint aerosol samples of Field Study I and from 12 µm to 32 µm in Field Study II. Figure 1 indicates that the MMAD averaged 7.5 µm (GSD = 2.7) for total Cr particles in Field Study I and 7.0 µm (GSD = 2.7) for total Cr particles in Field Study II.

The MMAD of Cr(VI) particles in paint samples of Field Study II ranged from 11 to 19 µm. It averaged 8.5 µm (GSD = 2.2) when cumulative mass fractions were averaged for each particle size range across paint aerosol samples (Table 3).

Carlton and Flynn (1997) investigated the breathing zone particle size distribution of an HVLP-generated paint aerosol in the field. They directly measured paint particle size with an optical microscope to minimize bias from solvent evaporation. They reported average MMDs of 18.9 and 14.8 µm, depending on the direction of the airflow in the spray booth with respect to the worker. In one of the booth set ups described by Carlton and Flynn, the airflow moved from the worker's back, past the work piece being painted and toward the booth exhaust baffles. The authors referred to this set up as the '180° position'. In this set up Carlton and Flynn reported an average MMD of 14.8 µm for paint aerosol. Three of the six paint spray booths sampled in this study (booths A, B and C) were similar to the set up of the '180° position'. These three booths resulted in total Cr MMADs between 9 and 20 µm. The MMADs of total Cr and Cr(VI) particles measured in this study are consistent with the MMD of paint aerosol reported by Carlton and Flynn (1997).

There was considerable variability in Cr aerosol MMADs of Field Studies I and II (Table 3). Several parameters may have affected paint aerosol size distributions. Carlton and Flynn (1997) had demonstrated that the worker's position relative to the airflow in a paint booth strongly influences breathing zone size distributions. There were four different booth designs and three different ventilation systems in this study (Table 5).

Paint composition is another factor that could have contributed to the observed variability in MMADs since five different paint products (Table 1) were used in this study. Different paint compositions may influence viscosity and resulting size distribution (Kim and Marshall, 1971; Ackley, 1980).

Atomization pressure at the spray gun nozzle has been shown to directly affect the size distribution of the aerosol it generates (Chan *et al*., 1986; Carlton and Flynn. 1997). The atomization pressure of each spray gun was unknown and may have differed from one gun to another.

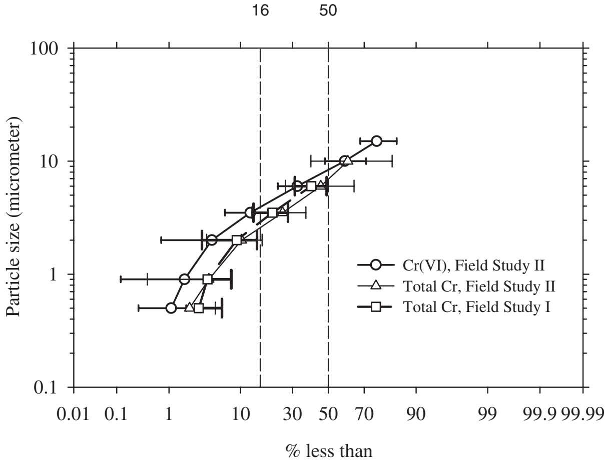
Evaporation of paint droplets could potentially cause an error in measured particle size distribution. Paint droplets leaving the spray gun were composed of solid-Cr-containing particles surrounded essentially by a solvent since powdered chromate salts were mixed with solvents, resin systems and catalysts to produce paint products (Table 1). The atomizing air transported paint droplets from the spray gun nozzle to the workpiece surface. During the transport process, some of the paint solvent evaporates with a concomitant decrease in paint droplet size. The size

Table 2. Mean percentage and standard deviation of Cr aerosol by size range

	Mass percentage (%) of Cr in specified size ranges[a]						
	<.5	.5–1	1–2	2–3.5	3.5–6	6–10	>10
Field study I							
Total Cr							
Booth A							
Mean	3.6	5.2	2.6	7.1	6.0	16.1	60.1
SD	5.0	3.4	3.6	1.8	5.8	1.1	15.3
Booth B							
Mean	2.4	0.7	0.8	9.1	16.3	19.4	51.4
SD	0.7	0.2	1.1	0.9	5.9	2.5	9.1
Booth C							
Mean	0.9	0.4	0.9	7.1	9.3	17.5	63.9
SD	1.6	0.3	1.0	5.0	2.3	7.4	13.2
Booth D							
Mean	0.5	0.3	0.6	4.0	11.9	24.1	58.6
SD	0.1	0.3	0.6	2.8	3.0	2.1	6.5
Booth E′							
Mean	1.3	0.1	0.3	3.5	16.6	21.8	56.3
SD	1.3	0.1	0.4	1.9	4.4	3.7	6.3
Booth E″							
Mean	2.9	1.3	1.0	2.9	9.5	16.4	66.0
SD	4.4	1.5	0.5	1.6	3.7	2.9	1.8

	Mass percentage (%) of Cr in specified size ranges[a]								
	<.5	.5–1	1–2	2–3.5	3.5–6	6–10	10–15	15–21	>21
Field Study II									
Total Cr									
Booth D									
Mean	0.9	0.1	0.2	0.8	6.0	19.0	25.0	18.7	29.3
SD	0.3	0.0	0.1	0.3	2.5	5.6	4.4	2.0	4.7
Booth E′									
Mean	1.8	1.1	0.3	3.0	8.9	14.4	18.1	15.5	36.9
SD	2.0	1.5	0.2	3.0	5.5	6.8	3.4	3.3	15.3
Booth E″									
Mean	0.5	0.4	0.2	1.4	8.5	18.6	23.7	17.5	29.2
SD	0.0	0.3	0.2	1.0	3.7	3.3	1.1	5.9	1.5
Booth F									
Mean	0.2	0.4	1.7	2.9	7.0	22.6	31.1	16.2	17.9
SD	0.1	0.6	2.4	2.5	1.6	3.0	6.5	2.3	3.7
Cr(VI)									
Booth D									
Mean	1.3	0.2	0.3	1.0	7.3	19.4	27.9	18.9	23.7
SD	1.1	0.2	0.1	0.4	3.1	2.8	5.7	2.8	5.4
Booth E′									
Mean	1.0	0.1	0.3	4.8	9.2	15.7	20.9	17.6	30.4
SD	0.7	0.0	0.2	5.7	5.6	6.0	2.2	4.0	12.2
Booth E″									
Mean	0.9	0.2	0.5	1.8	10.5	22.0	28.2	11.8	24.2
SD	0.5	0.1	0.3	1.6	6.8	6.9	4.2	15.7	4.8
Booth F									
Mean	0.2	0.4	1.7	2.8	6.9	22.8	31.4	16.4	17.5
SD	0.1	0.6	2.6	2.5	1.6	3.0	6.8	2.4	3.8

[a] Size ranges in μm.



[a]Horizontal bars represent one standard deviation around the mean

Fig. 1. Log probability graph of particle diameter by percentage of particle mass less than a given size[a].

Table 3. Average MMAD and average (GSD)[a] of Cr in field Studies I and II

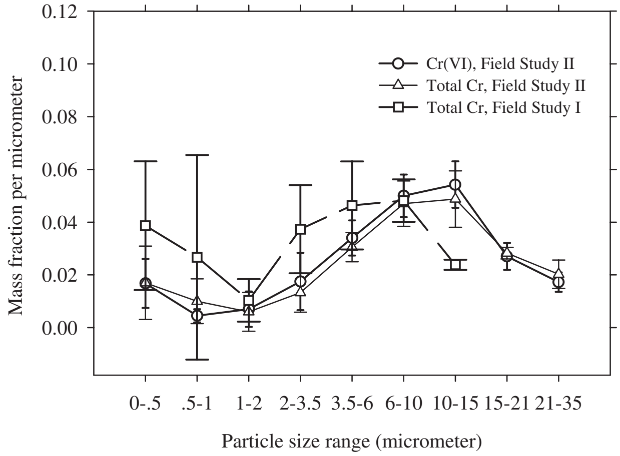
	Mean MMAD (μm)	Mean GSD	Range (μm)
Field study I			
Total Cr	7.5	2.6	9–40
Field study II			
Total Cr	12	2.7	12–32
Cr(VI)	8.5	2.1	11–19

[a]The GSD was estimated for the portion of the aerosol size distribution >2 μm.

distribution of paint spray aerosol continually changed as the aerosol changed from 'wet' to 'dry', and reached a steady size distribution after the evaporation of solvents was complete. In this study, paint spray was captured by cascade impactors in the breathing zone of workers. It was assumed that the aerosol captured by the cascade impactor is representative of the aerosol that would be inhaled by the worker wearing the cascade impactor. Particles impacted on the different stages of the cascade impactor based on their aerodynamic size as they traveled through the cascade impactor. The mass of Cr was measured on each impactor stage to evaluate Cr size distributions. Evaporation of paint solvents prior to entering the inlet of a cascade impactor, and after impaction, had no effect on the measured mass of Cr on each stage because the Cr was part of the solid fraction in the paint. Evaporation of solvents may have occurred as the paint aerosol traveled through the cascade impactor. This evaporation would change the measured size distribution if there is significant difference in fractional evaporation with particle size during the time from when a particle enters the impactor inlet to the time when it is deposited on an impactor stage. The authors do not believe this could cause a significant error in the measured particle size distribution because the average transit time in the impactor, ~0.2 s, is brief compared with the time for complete solvent evaporation, which more than a minute. Transit time in the impactor was estimated from the flow rate through the impactor and the calculated air volume inside the impactor. In addition, bulk paint products used in the booths evaluated in this study had a maximum solvent content of 75% by volume. If all the solvent evaporated from a paint droplet, the final diameter would be the cube root of (1–0.75), 63% of the original diameter. Thus a 10 μm particle exiting the paint spray gun will have a diameter of 6.3 μm after complete evaporation of all the solvents in the particle. Paint droplets were observed to be wet and sticky when they deposited in the cascade impactor. So, solvent evaporation was not complete at the time of deposition and could not have caused a significant error in the measured size distribution and their MMADs.

Differential size distributions of total Cr and Cr(VI)

Figure 2 depicts the normalized mass fraction/μm of total Cr for 16 samples of paint spray aerosol from Field Study I and 11 paint aerosol samples from Field Study II. The figure shows that Cr mass in Field Study I had a submicron fraction and a larger fraction between 3.5 and 10 μm. Cr mass in Field Study II consisted of a small fraction <0.5 μm in size and a larger fraction between 6.5 and 10 μm. Cr(VI) mass in Field Study II consisted of a small fraction <0.5 μm in size and a larger fraction between 6.5 and 15 μm (Fig. 2). Therefore, observed size distributions of total Cr and Cr(VI) particles in this investigation were multi-modal, in agreement with paint aerosol



^{a}Vertical bars represent one standard deviation around the mean

Fig. 2. Chromium particle size distribution in paint spray aerosol^{a}.

size distributions described by Ackley (1980), Kim and Marshall (1971) and Kwok (1991).

Cr(VI) to total Cr mass ratio

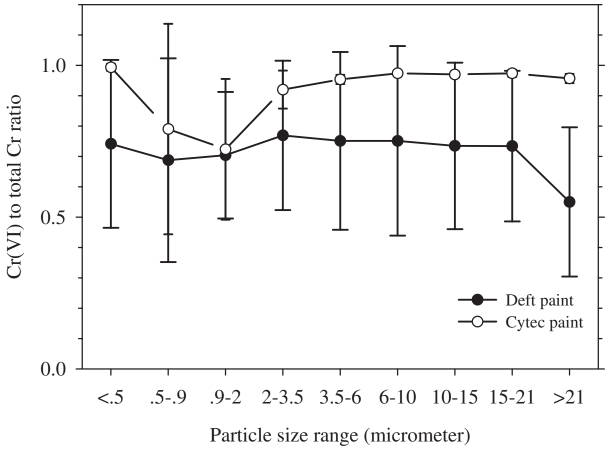
A comparison of Cr(VI) mass to total Cr mass ratios between different particle size ranges of paint aerosol samples showed that the size of particles does not affect the contribution of Cr(VI) relative to total Cr in paint spray aerosol. Figure 3 provides a graph of the ratio of Cr(VI) mass to total Cr mass for each particle size fraction averaged across samples. It shows that the average mass ratio of Cr(VI) to total Cr in different size fractions of paint aerosol samples ranged from 0.55 (±0.25) to 0.77 (±0.25) in 9 Deft paint aerosol samples and from 0.72 (±0.23) to 0.99 (±0.01) in 3 Cytec paint aerosol samples. There was no statistically significant difference between the smallest and largest mean Cr(VI) to total Cr mass ratio for Deft paint aerosol samples (p-value= 0.08) or Cytec paint aerosol samples (p-value = 0.31), in the different aerosol size fractions.

Cr in bulk paint products was predominantly in the Cr(VI) valence state. Two paint products (Deft and Cytec paints) were used in the spray booths evaluated in Field Study II. The average ratio of Cr(VI) mass to total Cr mass in bulk paint ranged from 0.98 (±0.02) to 1.00 (± 0.00) for 9 Deft paint samples taken from 3 paint booths. The average ratio was 0.96 (± 0.02) for bulk Cytec paint based on 3 bulk samples collected from one spray booth.

The data indicate there was significant reduction of Cr(VI) in Deft paint aerosol samples. The reduction was not related to Cr aerosol particle size. A comparison of Cr(VI)mass to total Cr mass ratios between bulk paint and sprayed paint aerosol showed a statistically significant difference for Deft paint (p-value << 0.05) but not for Cytec paint (p-value = 0.62). The Cr(VI) reduction occurred during or after sample collection since 96–100% of the Cr was in the Cr(VI) state in bulk paint samples, before the paint was sprayed. It is unlikely that Cr(VI) underwent reduction after sample collection, during sample transportation or up to the beginning of sample preparation because samples were refrigerated during that time period. The stability of Cr(VI) in refrigerated paint samples has been reported by Molina and Abell (1987) and Sabty-Daily *et al.* (2002). Sample preparation and analysis methods are not likely to have affected Cr(VI) reduction during sample analysis since these methods have been validated for the quantitative analysis of Cr(VI) (NIOSH, 1994b; U.S. EPA, 1996b; California EPA, 1997; Sabty-Daily *et al.*, 2002). Cr(VI) reduction must have then occurred during the 8 h sample collection time period of Deft paint aerosol. These findings are in agreement with the findings by other authors who observed Cr(VI) reduction, during collection of airborne Cr(VI) in samples of chromic acid mist (Research Triangle Institute, 1988; Shin and Paik, 2000) and welding fumes of chromium alloy steels (Gray, 1983).

Respiratory deposition of total Cr and Cr(VI) aerosol

Table 4 provides the mean percentage of Cr aerosol deposited in the head airways, tracheobronchial and alveolar regions of the respiratory system. The estimated percentage of total Cr and Cr(VI) aerosol in the different respiratory sites was calculated based on measured mass distributions. The major deposition site of total Cr and Cr(VI) particles potentially inhaled by the spray painters under the study was the head airways region. The fraction of total Cr and Cr(VI) expected to deposit in different regions of the respiratory tract was estimated. In Field Study I, the largest portion of the aerosol, an average of 65.7%, was estimated to deposit in the head airways.



[a]Vertical bars represent one standard deviation around the mean

Fig. 3. Cr(VI) to total Cr ratio by particle size in paint aerosol samples[a].

Table 4. Estimated Mean Percentage (SD) of Cr aerosol deposition in the head airways, tracheobronchial and alveolar regions

Booth	Head airways region			Tracheobronchial region			Alveolar region		
	Field study I	Field study II		Field study I	Field study II		Field study I	Field study II	
	Total Cr	Total Cr	Cr(VI)	Total Cr	Total Cr	Cr(VI)	Total Cr	Total Cr	Cr(VI)
A	60.4 (0.7)	–	–	1.3 (0.6)	–	–	2.6 (1.1)	–	–
B	67.5 (2.3)	–	–	1.9 (0.4)	–	–	2.9 (0.4)	–	–
C	65.5 (2.2)	–	–	1.4 (0.5)	–	–	2.1 (0.9)	–	–
D	68.1 (1.2)	70.3 (1.2)	71.2 (0.2)	1.4 (0.3)	1.1 (0.2)	1.2 (0.2)	2.0 (0.5)	1.5 (0.2)	1.7 (0.3)
E′	68.4 (2.0)	67.5 (4.4)	73.0 (2.5)	1.6 (0.2)	1.2 (0.5)	1.5 (0.5)	2.2 (0.3)	1.9 (0.9)	2.1 (0.6)
E″	63.2 (3.3)	70.7 (1.4)	72.7 (3.5)	1.1 (0.1)	1.2 (0.3)	1.5 (0.6)	1.9 (0.2)	1.7 (0.4)	2.0 (0.8)
F	–	73.1 (1.4)	73.2 (1.5)	–	1.5 (0.2)	1.4 (0.2)	–	3.9 (2.4)	2.1 (0.4)
All booths	65.7 (3.3)	70.5 (3.0)	71.8 (2.4)	1.4 (0.4)	1.3 (0.3)	1.4 (0.3)	2.2 (0.6)	2.3 (1.5)	2.0 (0.5)

Field Study II similarly showed that an average of 70.5% of the total Cr mass and 71.8% of the Cr(VI) mass in the sampled paint aerosols may deposit in the head airways. Study results showed that 2.2% of the total Cr mass and 2.0% of the Cr(VI) mass potentially inhaled by a paint sprayer could deposit in the alveolar region of the respiratory system. The least likely deposition site for inhaled Cr and Cr(VI) from spray paint was the tracheobronchial region where only ~1.4% of the total Cr and Cr(VI) aerosol mass could potentially deposit.

Particles deposited in the respiratory system are subjected to various biological, physical and chemical processes including dissolution into body fluids with absorption by the blood, uptake into cells by phagocytosis and movement with mucus and body fluids (Raabe, 1999). These processes vary from one region of the respiratory system to another, therefore affecting the clearance and retention of particles deposited in these different regions. This study showed that 71.8% of Cr(VI) mass in the sampled paint aerosols may deposit in the head airways region.

Airborne total Cr and Cr(VI) concentrations

Airborne Cr and Cr(VI) concentrations were measured in the process of collecting particle size distribution and speciation data of paint aerosol. Table 5 lists the TWAs for total Cr and Cr(VI) exposures in paint spray booths of Field Studies I and II. In Field Study I, the highest mean total Cr airborne concentration was 256 μg/m^3 in 1 out of 6 sampled spray booths. In Field Study II, the highest mean total Cr airborne concentrations ranged from 196 to 332μg/m^3 in 3 out of 4 sampled spray booths. Assuming most of the Cr in the paint is in the Cr(VI) form, workers in these spray booths were potentially exposed to airborne Cr(VI) concentrations greater than the Occupational Safety and Health Administration (OSHA) Permissible Exposure Limit (PEL) of 100 μg/m^3 for insoluble chromates (CFR, 2000). The Cr(VI) air concentrations in Field Study II ranged from 19 to 327 μg/m^3. The highest mean Cr(VI) air concentrations were measured in booth D, 214 μg/m^3, and booth F, 190 μg/m^3. The Cr(VI) airborne concentrations of 3 out of 4 sampled painters were

Table 5. 8 h TWA for Cr exposures in paint booths

Booth	Booth type	8 h TWA ($\mu g/m^3$)[a]								
		Field study I			Field study II					
		Total Cr			Total Cr			Cr(VI)		
		Range	Mean	N	Range	Mean	N	Range	Mean	N
A	Open/back-wall exhaust	1.0–9.5	5.3	3	–	–	0	–	–	0
B	Open/back-wall exhaust	4.8–5.7	5.3	3	–	–	0	–	–	0
C	Open/back-wall exhaust	4.7–8.2	6.5	3	–	–	0	–	–	0
D	Enclosed/down draft	177–364	256	3	289–390	332	3	69–327	214	3
E′	Open/down draft	20–123	57	3	22–83	56	3	19–125	70	3
E″	Open/down draft	11–38	23	3	205–302	253	3	65–275	170	3
F	Enclosed/down draft	–	–	0	138–273	196	3	134–265	190	3

[a] Occupational Safety and Health Administration (OSHA) Permissible Exposure Limit (PEL): 100 $\mu g/m^3$ for insoluble chromates (CFR, 2000b).

greater than the OSHA PEL of 100 $\mu g/m^3$ for insoluble chromates.

In both Field Studies, workers wore respirators at the time of sampling and this would have significantly decreased their exposures to total Cr and Cr(VI). Painters exposed to the highest airborne concentrations of Cr in Field Study I, were sprayers in booths equipped with a down-draft/water-wash ventilation system (Table 4). This data indicated that down-draft/water-wash ventilation systems might be less efficient than back-wall exhaust systems at removing spray aerosol from the worker's breathing zone. This finding is not consistent with the results of a study by Heitbrink *et al.* (1995) who investigated the control of paint overspray in autobody shops. The study concluded that downdraft spray-painting booths minimize overspray exposure better than crossdraft or semi-downdraft booths. The authors attributed the efficiency of the studied downdraft booths to their ability to move overspray away from the worker toward the exhaust before the overspray mixes with the incoming fresh air. They also noted that exposure to overspray occurred in downdraft booths when overspray is inadvertently directed toward the worker. In this study, workers sprayed large pieces of airplane fuselage (10′ h × 20′ l) in the downdraft booths. The painters moved their arm up and down to spray the fuselage while slowly walking forward along the side of the fuselage. Their breathing zone was often between the overspray and the exhaust. The overspray was generally visible in the worker's breathing zone. The worker wore overalls with a hood as well as a full-face-air-purifying respirator during spraying. The hood as well as the rest of the overalls and respirator were typically covered with paint after spraying due to the overspray reaching the worker before it was removed toward the exhaust. Therefore, design of a ventilation booth is only one of the factors that affect exposure of workers to paint overspray in paint booths. Other parameters that affect the exposure of a worker to overspray during spray painting are size and shape of the part being painted and movement of the worker's hand, arm and body as she or he applies the paint.

Limitations

Interpretation of the observed paint aerosol size distributions was limited by the use of cascade impactors as sampling devices. The cascade impactor collected the total aerosol mass but had a cut off for the first stage a diameter of 10 μm, in Field Study I, and 21 μm in Field Study II. Therefore, it could not classify the part of the aerosol size distribution greater than these cut-off diameters. Rubow *et al.* (1987) evaluated the Marple cascade impactor used in this study for sampling efficiency. They reported a decrease in the sampling efficiency of the cascade impactor for particles >7 μm in diameter; sampling effectiveness was 84% for 10 μm particles and ~60% for 20 μm particles. Therefore, we cannot infer the specific shape of the size distribution of Cr particles in the size range >10 μm for Field Study I and >21 μm for Field Study II.

CONCLUSION

The mass of total Cr and Cr(VI) in paint aerosol samples of two field studies consisted primarily of particles >10 μm. Seventy-two percent of Cr(VI) mass in paint spray aerosol potentially inhaled by a spray painter may deposit in the head airways region. Further research is required on the bioavailability and clearance of Cr and Cr(VI) to further define the toxicokinetics and dosimetry of the compounds within the epoxy matrix of paint. Cr(VI) reduction has been observed during paint aerosol sampling. The use of Cr(VI) stabilizing sampling media and maintaining samples at lower temperatures is likely to result in more accurate assessment of airborne concentration levels of Cr(VI) from paint spray exposures.

Disclaimer. Mention of company trade names or products does not constitute endorsement by the University of California, Los Angeles or the California State University, Los Angeles.

Acknowledgements—We sincerely thank the management and workers of the Aircraft Division of Northrop Grumman Corporation, Hawthorne, California for participating in this study. Ms Scotty Butler and Ms Jackie Lucas at the Northrop Grumman Corporation in Hawthorne, California, made this study possible with their persistent efforts and support. Ms Pamela Yates provided valuable input. Dr Yoram Cohen and Dr Wen Chen Liu reviewed the manuscript. Mr Gustavo Cordero and Ms Kanugnig Thirakomen provided laboratory technical assistance. Health Science Associates in Los Alamitos, California, performed Cr(VI) and total Cr analysis of paint samples. Deft Inc., supplied paint materials and information. Partial funding was received from the National Institute for Occupational Safety and Health grant U60 CCU902886, the Toxic Substances Research and Teaching Program of the University of California, the Center for Occupational and Environmental Health of the University of California in Los Angeles, the Public Health Trust grant 543A 8802 G1298 and the National Institute for Occupational Safety and Health Education and Research Center grant 742/CCT918726. The study was supported by the National Institute of Environmental Health Sciences grant 5 P30 ES07048-06.

REFERENCES

Ackley MW. (1980) Paint spray tests for respirators: aerosol characteristics. Am Ind Hyg Assoc J; 41: 309–316.

ATSDR. (1993) Toxicological profile for Chromium. Prepared by Syracuse Corp. under contract no. 205-88-0608. Atlanta, GA: Agency for Toxic Substances and Disease Registry, U.S. Department of Health and Human Services.

Alexander BH, Checkoway H, Wechsler L *et al*. (1996) Lung cancer in chromate-exposed aerospace workers. J Occup Med; 38: 1253–1258.

ACGIH. (1995) Particle size-selective sampling in the workplace: report of the ACGIH technical committee on air sampling procedures. Cincinnati, OH: American Conference of Governmental Industrial Hygienists. pp. 65–76.

Brinton L, Blut WJ, Becker JA *et al*. (1984) A case-control study of cancers of the nasal cavity and paranasal sinuses. Am J Epidemiol; 119: 896–906.

California EPA. (1997) Determination of total chromium and hexavalent chromium: emissions from stationary sources (Method 425). California Air Resources Board, California Environmental Protection Agency.

Carlton GN, Flynn MR. (1997) Influence of spray painting parameters on breathing zone particle size distributions. Appl Occup Environ Hyg; 12: 744–750.

Chan TL, D'Arcy JB, Schreck RM. (1986) High-solids paint overspray aerosols in a spray painting booth: particle size analysis and scrubber efficiency. Am Ind Hyg Assoc J; 47: 411–417.

Chiazze LJr, Ferrence LD, Wolf PH. (1980) Mortality among automobile assembly workers. I. Spray painters. J Occup Med; 22: 520–526.

CFR. (2000) 29 CFR Part 1915.1000. Subpart Z: toxic and hazardous substances, Washington, D.C: United States Government Printing Office, Code of Federal Regulations.

Dalager NA, Mason TJ, Fraumeni JF Jr *et al*. (1980) Cancer mortality among workers exposed to zinc chromate paints. J Occup Med; 22: 25–29.

Dyg S, Anglov T, Christensen JM. (1994) Preparation of filters loaded with welding dust; a homogeneity and stability study of hexavalent chromium. Anal Chim Acta; 286: 273–282.

Gibb HG, Lees PSJ, Pinsky PF *et al*. (2000) Lung cancer among workers in chromium chemical production. Am J Ind Med; 38: 115–126.

Gorner P, Fabries J-F. (1996) Industrial aerosol measurement according to the new sampling conventions. Occup Hyg; 3: 361–376.

Gray CN, Goldstone A, Dare PRM *et al*. (1983) The evolution of hexavalent chromium in metallic aerosol. Am Ind Hyg Assoc J; 44: 384–388.

Heitbrink WA, Wallace ME, Bryant CJ *et al*. (1995) Control of paint overspray in autobody repair shops. Am Ind Hyg Assoc J; 56: 1023–1032.

Hinds WC. (1986) Data analysis. In: Lodge JPJr, Chan TL, editors. Cascade impactor: sampling and data analysis, Akron, OH: American Industrial Hygiene Association. pp. 45–78. ISBN 0 932627 24 2

Hinds WC. (1999) Aerosol technology, properties, behavior, and measurement of airborne particles. 2nd edn. New York, NY: John Wiley & Sons Inc. pp. 233–259. ISBN 0 471 19410 7.

IARC. (1990) IARC monographs of the evaluation of the carcinogenic risk of chemicals to humans: chromium, nickel and welding. Lyon, France: International Agency for Research on Cancer, Vol. 49.

ICRP. (1994) Human respiratory tract model for radiological protection. In: Annals of the ICRP. Tarrytown, NY: Elsevier Science, International Commission on Radiological Protection, Pub. No. 66.

Kim KY, Marshall WR Jr. (1971) Drop-size distributions from pneumatic atomizers. Am Institute Chem Engineers; 17: 575–584.

Kroschwitz, J. (1994) Epoxy resin. In: Encyclopedia of chemical technology. New York: John Wiley & Sons.

Kwok K. (1991) A fundamental study of air spray painting. Ph.D. dissertation. University of Minnesota, Minneapolis, MN.

Langard S. (1990) One hundred years of chromium and cancer: a review of epidemiological evidence and selected case reports. Am J Ind Med; 17: 189–215.

Lees PSJ. (1991) Chromium and disease: review of epidemiologic studies with particular reference to etiologic information provided by measures of exposure. Environ Health Perspect; 92: 93–104.

Lippmann M, Yeates DB, Albert RE. (1980) Deposition, retention and clearance of inhaled particles. Br J Ind Med; 37: 337–362.

Losi ME, Amrhein C, Frankenberger WTJr. (1994) Environmental biochemistry of chromium. Rev Environ Contam Toxicol; 136: 91–121.

Molina D, Abell MT. (1987) An ion chromatographic method for insoluble chromates in paint aerosol. Am Ind Hyg Assoc J; 48: 830–835.

NIOSH. (1973) Criteria for a Recommended Standard- Occupational Exposure to Chromic Acid (HSM 73-11021). Cincinnati, OH: National Institute for Occupational Safety and Health.

NIOSH. (1994a) NIOSH manual of analytical methods, 4th edn (Method 7024). Cincinnati, OH: DHHS, National Institute for Occupational Safety and Health, Pub. No. 14–113

NIOSH. (1994b) NIOSH manual of analytical methods, 4th edn (Method 7604). Cincinnati, OH: National Institute for ccupational Safety and Health, Pub. No. 14–113

OSHA. (1998) Hexavalent chromium in workplace atmospheres, Inorganic Method 215. Occupational Safety and Health Administration, U.S. Department of Labor.

Raabe, OJ. (1999) Respiratory exposure to air pollutants. In: Swift DL, Foster W.M, editors. Air pollutants and the respiratory tract, New York, NY: Marcel Dekker, Inc. ISBN 0 8247 9521 0.

Research Triangle Institute. (1998) The Fate of Hexavalent Chromium in the Atmosphere. A report to California Air Resources

Board, Research Triangle Park, NC, Research Triangle Institute. RTI/3798/00-01F.

Rubow KL, Marple VA, Olin J *et al*. (1987) Personal cascade impactor: design, evaluation and calibration. Am Ind Hyg Assoc J; 48: 532–538.

Sabty-Daily RA, Luk KK, Froines JR. (2002) 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. Analyst; 127: 852–858.

Sherwell J, Silvers M. (1992) The extraction and analysis of chromium (VI) in soils and sludges. A report to the U.S. Environmental Protection Agency (Task 3A).

Shin YC, Paik NW. (2000) Reduction of hexavalent chromium collected on PVC filters. Am Ind Hyg Assoc J; 61: 563–567.

Spini G, Profumo A, Riolo C *et al*. (1994) Determination of hexavalent, trivalent and metallic chromium in welding fumes. Toxicol Environ Chem; 41: 209–219.

U.S. EPA. (1983) Methods for chemical analysis of water and wastes (Method 218.2). NTIS, Springfield, VA: U.S. Environmental Protection Agency, Pub. No. PB84-128677

U.S. EPA. (1984) Health assessment document for chromium. Washington D.C.: U.S. Environmental Protection Agency, Pub. No. 600/8-83-014F.

U.S. EPA. (1991) Method 218.6: Determination of dissolved hexavalent chromium in drinking water, groundwater and industrial wastewater effluents by ion chromatography. 3rd rev by E.J. Arar, S.E. Long, and J.D. Pfaff. Cincinnati, OH: U.S. Environmental Protection Agency.

U.S. EPA. (1996a) Test methods for evaluating solid waste: physical/chemical methods, 3rd edn (Method 6010B). NTIS, Springfield, VA: U.S. Environmental Protection Agency, Pub. No. PB98-111750.

U.S. EPA. (1996b) Test methods for evaluating solid waste: physical/chemical methods, 3rd edn (Method 7196A). NTIS, Springfield, VA: U.S. Environmental Protection Agency, Pub. No. PB98-111750.