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Chromium Concentration Bias in the Particle Size Distribution of Primer Overspray

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CHROMIUM CONCENTRATION BIAS IN THE PARTICLE SIZE DISTRIBUTION OF PRIMER OVERSPRAY

THESIS

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AFIT/GEE/ENV/00M-06

DEPARTMENT OF THE AIR FORCE
AIR UNIVERSITY
AIR FORCE INSTITUTE OF TECHNOLOGY

Wright-Patterson Air Force Base, Ohio

Disclaimer Statement

AFIT/GEE/ENV/00M-06

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THESIS

Presented to the Faculty of the Graduate School of Engineering and Management
Of the Air Force Institute of Technology
Air University
In Partial Fulfillment of the
Requirements for the Degree of
Master of Science in Engineering and Environmental Management

Joseph M. Fox
Captain, USAF

March 2000

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Abstract

Air Force aircraft-painting operations create clouds of paint overspray that contain strontium chromate, a confirmed carcinogen, which poses an exposure hazard to painters. It is often assumed that all particles in paint overspray have the same chemical composition as the original paint mixture, however differences in composition may occur in various particle sizes. Because particle size affects where in the respiratory system a particle deposits, actual exposures to a specific chemical may vary. Paint particles greater than 2.5 um are deposited in the upper respiratory system and will be eliminated by physiological removal mechanisms. Particles less than 2.5 um will deposit in the pulmonary region of the lungs where removal processes are slower. Currently it is assumed for the purposes of industrial hygiene evaluations that there is an equal distribution of chromate across all paint particle sizes.

Particle size distributions were collected on digestible cellulose substrates during painting operations using two 7-stage cascade impactors. Each substrate was weighed before and after collection to determine total mass collected at each particle size and then samples were digested and analyzed for chromium mass by atomic absorption spectrometry. In particles smaller than 2.5 um, chromium concentrations per total mass collected averaged 21 ug of chromium/ mg of total mass collected. Particles larger than 2.5 um averaged 75 ug/mg. A Wilcoxin ranked sum test was used to evaluate the two data groups and found a statistically significant difference between the two particle size groups, indicating that less chromium is found in particles most likely to deposit reach the pulmonary region of the lungs. The data also showed that 94 percent of the total chromium mass collected was contained in particles greater than 2.5 um.

The results of this experiment show that theoretical exposure calculations, which assume the composition of a paint particle is equal to the original paint mixture, may overstate actual exposures. The results of this study also provide evidence that the concentration and mass of chromium deposited in the pulmonary region of the lungs may be significantly less than what is deposited in the upper regions. This leads to the conclusion that pulmonary dosing is less of an exposure hazard than would be concluded by assuming an equal distribution of chromium across all particle sizes.

CHROMIUM CONCENTRATION BIAS IN THE PARTICLE SIZE DISTRIBUTION OF PRIMER OVERSPRAY

I. Introduction

Background

Current global conflicts and the dynamic mission of the U.S. Air Force requires that Air Force aircraft be capable of operation in any environment from arctic bases to desert warfare. Any operational environment will subject the aircraft skin to natural chemical processes such as the formation of aluminum oxide corrosion on the aircraft skin which weakens the integrity of the skin and can reduce it's useful life. Protecting aircraft surfaces from these hostile environments is one of the most important elements in maintaining the structural integrity and function of the aircraft (T.O. 1-1-8, 1989).

To prevent corrosion, aircraft are coated with a corrosion resistant layer, the primer coat, to protect the aircraft skin from the effects of adverse environmental conditions (Figure 1). The primary mechanisms for corrosion protection are chromate salts in the primer. A commonly used salt is strontium chromate, which is bound within the primer matrix. This matrix is designed to release the chromate from the polymer matrix as the aircraft paint flexes and cracks during operation or is scratched by mechanical means. The chromate particles leach out of the primer matrix and flow into small cracks that may form in the aircraft skin. The slightly water-soluble chromate (1.2 g/l at 15° C (Weast, 1985)) migrates to the area of damage which helps prevent the formation of aluminum oxide (similar to rust on an iron surface).

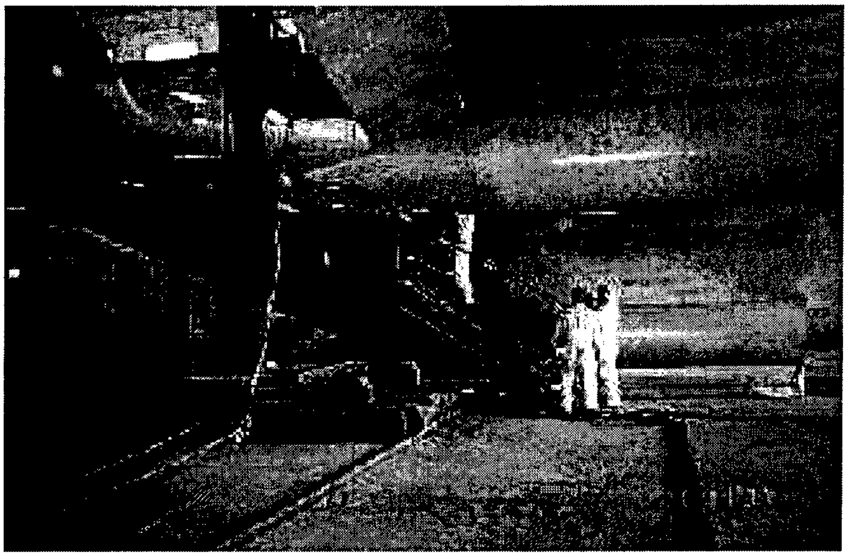


Figure 1. Air Force Primer Application Operation

The Air Force controls the quality and composition of these primers by providing paint manufacturers with military specifications that specify the corrosion protection requirements of these primers. Ongoing research efforts are attempting to find replacements for chromates, but the most effective primers currently rely on chromate-based formulas to meet the corrosion protection requirements.

Table 1 lists the four current military specifications for primers authorized for use on Air Force aircraft (T.O. 1-1-8, 1989).

Table 1. Air Force Primers

Military Specification Number	Primer Type	Notes
MIL-P-23377	Epoxy polyamide	Excellent adhesion properties, brittle compared to other primers
MIL-P-85582	Water based	Limited use
TT-P-2760	Polyurethane	Excellent flexibility
MIL-P-87112	Polysulfide	High Volatile Organic Compounds (VOCs), very flexible

Currently MIL-P-23377 is the most widely used primer paint based on its highly effective adhesion and protection characteristics (Weissling, 1996:62). MIL-P-23377 is an epoxy-polyamide, two part coating that addresses the Air Force's requirements for a chemical and solvent resistant primer. The requirements addressed by this specification require a minimum degree of corrosion protection for metal surfaces. There are characteristics which are desirable in primers but are traded off for more important properties. Flexibility is a desirable characteristic of a paint on aircraft due to a planes constant flexing during flight, but current primers that offer superior flexibility suffer from adhesion problems and lack of hardness that cannot offset the adhesion and hardness offered by MIL-P-23377 primers.

Large-scale application of paints occurs in Air Force industrial paint booths approved by the Occupational Safety and Health Administration (OSHA) that vary in size and design according to their mission. One common ventilation design provides an airstream, at a velocity of 100-150 feet per minute supplied by blowers at one end of the booth which carries the overspray out of the painter's breathing zone to a bank of filters lining the downwind wall of the booth. The actual configuration of the filter banks and their method of operation may vary from facility to facility, but all are required to meet federal standards.

Primers are applied using a variety of atomizing spray equipment that deposit a uniform coat of primer on the aircraft skin with a 0.6 mm - 0.9 mm thickness (T.O. 1-1-8, 1989). The Air Force has recently migrated to using High Volume Low Pressure (HVLP) spray equipment operating at 3-6 pounds per square inch (psi) which has paint transfer efficiency rates of approximately 50 – 80%. More traditional painting operations use high pressure systems operating at 60-80 psi which have efficiency rates of approximately 30 - 50% (Marg 1992). These transfer efficiency rates are based on laboratory tests and can be affected by several factors including the application technique. Depending on the size of the aircraft, teams of two, three, or even eight workers can be painting an aircraft at one time and often can be downwind of at least one other worker.

During primer application, a portion of the paint sprayed at the aircraft skin does not impact and adhere to the surface and becomes overspray which is a cloud of chromate-containing paint particles that can enter the painter's breathing zone despite the booth's ventilation capabilities. Hexavalent chromium compounds, including strontium chromate which is carcinogenic (IARC, 1990), are the primary forms of chromium in MILSPEC primers. These hexavalent chromium compounds have very low exposure standards set by OSHA and ACGIH based on their potential health effects.

There are several agencies that attempt to determine the maximum level at which workers can be exposed to a hazardous material with no adverse health effects. The National Institute for Occupational Safety and Health (NIOSH) sets Recommended Exposure Limits (RELs) for hazardous materials (NIOSH, 1998), OSHA sets Permissible Exposure Limits (PELs), and the American Conference of Government Industrial Hygienists (ACGIH) sets Threshold Limit Values (TLVs) (ACGIH, 1998). The Air Force may also set exposure limits for hazardous materials in certain cases but enforces the lowest exposure limit set by ACGIH, OSHA or the Air Force. NIOSH RELs are not followed. The 8-hour time weighted average exposure limit for strontium chromate has been set at 0.0005 mg/m^3 by ACGIH (ACGIH TLVs, 1998) and a ceiling exposure limit of 0.1 mg/m^3 has been set by OSHA (OSHA, 1997).

The current ACGIH strontium chromate standard is based on an experimental investigation of the effect of several chromate salts on laboratory rats (ACGIH TLV Documentation, 1998). Cholesterol pellets dosed with several chromate salts were implanted in the bronchi of rat lungs and were examined for the occurrence of bronchial carcinomas following a period of two years. The groups exposed to strontium chromate produced 43/100 and 62/100 bronchial carcinomas in two different study groups. These highly significant results were over twice the incidents of carcinomas of any other exposure group (Levy, 1986).

In addition to the low exposure limits for strontium chromate, the regulatory agencies assume a maximum effectiveness of respirators by applying an Assigned Protection Factor (APF) that sets an upper limit on the concentration, above which, respiratory protection is presumed inadequate to protect the worker. Most large scale painting operations in the Air Force use full-face air-supplied respirators operating in pressure demand which has an APF of 2,000 set by OSHA (OSHA RPA, 1999) and an APF of 1,000 set by the Air Force (AFOSH 48-137, 1998: 42).

OSHA has recently proposed implementing a 0.0005 mg/m^3 8-hour time weighted average which is a significant drop from the current 0.1 mg/m^3 standard (Federal Register 64:21485, 1999). Applying the APF of 1,000 and 2,000 respectively, this would set a maximum exposure concentration of 0.5 mg/m^3 (Air Force APF) and 1.0 mg/m^3 (OSHA APF) for operations requiring full-face air-supplied respirators operating in pressure demand mode. Air Force policy directs the use of the most restrictive protection factors, which would correspond to the 0.5 mg/m^3 exposure standard. There is evidence that Air Force painting operations currently exceed this concentration (LaPuma, 1999), which would result in violation of federal regulations if the proposed OSHA standard is implemented. This could result in impractical respiratory protection requirements in large-scale military painting facilities or effectively ban the use of strontium chromate primers in certain applications for which there is currently no suitable substitute.

Problem Statement

The studies that have been the basis for the strict chromate standards may not accurately reflect the actual chromate exposures seen in the Air Force and may significantly overstate the exposure potential for painters.

There are several exposure pathways by which a material may enter the body: inhalation, ingestion, contact, and absorption. Depending on the particular route of exposure, the body will fight the insult in a unique manner and the potential biological effects are determined by many factors including the final deposition of the material.

The exposure assessment for hexavalent chromium by inhalation is complicated by the ability of the respiratory tract to prevent certain particles (>10 μm) from reaching the bronchial region and the ability to eliminate particles (<10 μm and >2.5 μm) from the bronchial region via mucociliary transport. These particles are generally trapped in mucous, which will be transported out of the respiratory system within several days and may be processed in the gastrointestinal tract. Only the particles less than 2.5 um will reach the alveolar region where phagocytic cells will breakdown the paint matrix and the carcinogenic initiation may occur (Ballantyne, 1995:25).

Currently it is assumed that the distribution of chromium is consistent across all respirable particle sizes of primer overspray. If there is a disproportionate amount of chromium in overspray particles larger than 2.5 μm, then the actual lung pathway exposure to painters may be lower than currently assumed since these larger particles will not reach the deeper regions of the lung.

Research Question

The research question that this thesis will attempt to answer is:

> Is there a bias in the chromium concentration among various particle sizes of aircraft primer overspray?

This will be accomplished by sampling a painting operation and separating paint particles based on size. Each particle size bin will be analyzed for chromium concentration. A particle size bin is a collection of particles separated into groups according to size (Figure 2).

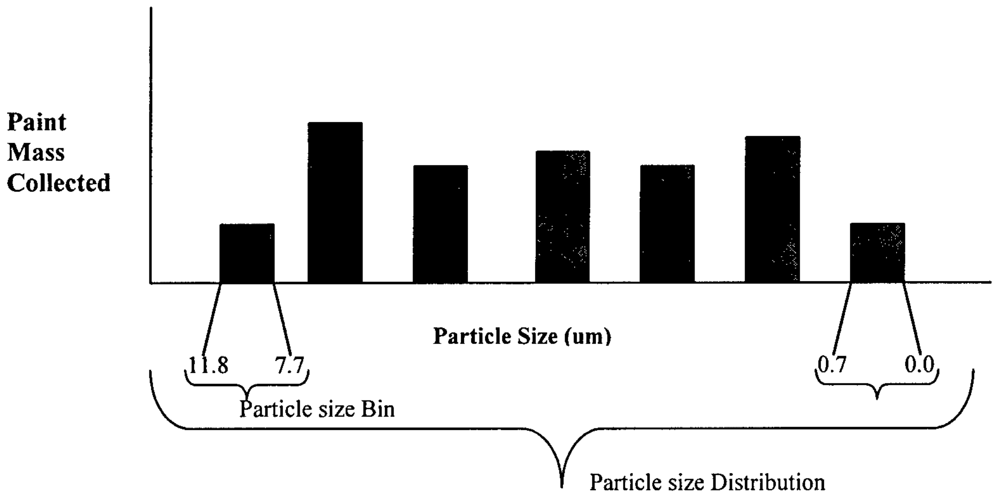


Figure 2. Theoretical Particle Size Distribution

The chromium concentration is based upon a ratio of chromium mass to the total dry mass of the paint. Statistical analysis will be used to evaluate differences in the chromium concentration between bins.

Assumptions/Limitations

Sampling Locations

Accurately characterizing the particle size distribution of overspray in the painter's breathing zone can be complicated by many variables. This study will approximate the downwind particle size distribution of overspray and ignore potential comparisons with the particle size distribution in the worker's breathing zone.

Chromium concentrations found in this study may be integrated with accurate breathing zone distributions as a follow on effort to determine more accurate exposures.

Collection Efficiency

This study focused on determining the concentration of chromium in collected paint particles. The measurement of chromium was not dependent on the collection efficiency of the sampling equipment.

Physical State of Samples During Analysis

Several previous studies have attempted to characterize the distribution of wet particles collected during painting operations. The results of these studies have been questioned due to the evaporation of the solvent component of the particles during and after sampling. This study will focus on the dry mass of the samples in order to create a consistent and reliable measure of the primer. The samples will be dried in a desiccator for 48 hours and weighed before and after sample collection. This will eliminate mass fluctuations caused by solvents and moisture.

II. Literature Review

Several areas of research are relevant to the work presented in this thesis. Previous research on overspray particle size distribution measurement and collection methods is reviewed to evaluate potential measurement methods that can satisfy our need to physically collect paint overspray and collect particles in relevant size ranges. The choice of sampling media is important to the effectiveness of collection and analysis. There are a variety of sampling media that can be used to collect the primer overspray. Previous research is evaluated to determine the optimal media for collecting the primer, based upon the sampling device and the analysis procedures.

The particles collected during painting are highly dependent upon the location of the sampling device with respect to the painter and the target. Research on location of sampling devices is examined to determine the optimal setup given our objectives. Environmental conditions can affect the characteristics of paint during flight which will affect the samples collected. Previous efforts are examined to understand the effects of environmental conditions on this effort.

The behavior of the sample after it is collected can alter the success of analysis. Preservation techniques are evaluated to understand evaporative effects on the samples. Following collection and preservation, the samples must be prepared for analysis. Digestion of the samples following collection is important to liberating the maximum amount of chromium for Atomic Absorption Spectrometry (AAS). Both research and regulations are evaluated for application to this effort. Research on the understanding of particle deposition in the lungs is also reviewed to expand the understanding of the impact of particle size characteristics on deposition in the lungs

Particle Size Distribution Measurement

There were to be two lines of research focus found for paint-overspray sampling: total particle size distributions and solvent content in overspray. These research efforts addressed both the automotive and aerospace industry. No research has specifically addressed primer coatings for aircraft. Primer coatings behave similarly to topcoats in aerosol behavior, but differ in composition since primers contain the chromate compounds that are of interest to this effort. Research has been performed that evaluates solvent components in primer paint-overspray, but has not addressed the concentration of chromates in paint-overspray based on particle size distributions.

One recent method for measuring particle size distributions is to acquire a "footprint" of the aerosol particle as it impacts on a substrate. This method attempts to reduce the bias caused by solvent evaporation when standard gravimetric techniques are used. Particles are collected on a Nyebar-treated polycarbonate filter and are viewed following sampling with an optical microscope equipped with image processing software which counts and sizes the droplets (Carlton et al, 1997). Considerations must be made for spreading of the aerosols on impact but this method has been shown to produce a highly correlated (r^2 =.998) relationship between the particles generated by a monodisperse aerosol generator and measured particle sizes. This method presents an approach that, while effective, does not allow for collection of the particles for further analysis and was not suitable for this effort.

Cohen et al, 1992 measured air concentrations of volatile components by sampling automotive topcoats and clearcoats as part of an investigation evaluating whether traditional vapor sampling techniques provide reliable estimates of inhalation exposures. This investigation did not include cascade impactors, a commonly used device for collecting particles based on size, and did not address particle size distributions. The results showed that aerosol droplets contained up to 50 percent of the measured airborne solvent, but this study did not provide any information on the solvent fraction in aerosol droplets that could have provided insight into the solid/liquid ratio of airborne particles.

Follow on work measured aerosol particle size distributions as part of an effort to evaluate total inhalation exposure from paint solvents (Brosseau et al, 1992: 610). Automotive coatings were sampled in an assembly paint booth using 4 and 6 stage cascade impactors with stainless steel substrates and were analyzed by weighing the samples. Results from the study showed a particle size distribution of 19 to 46 um with a Geometric Mean Aerodynamic Diameter (GMAD) of 23.9 um for personal samples, and a distribution of 22 to 26 um with a GMAD of 21.2 at the test stands. These particle size distributions provide a reference data set for particle size distributions in painting operations.

Chan et al, 1986 evaluated paint-overspray size distributions and paint booth effectiveness in an automotive industry setting using 7 stage cascade impactors. The primary focus of the study was to evaluate the efficiency of emission controls used in automotive paint booths. This required generation of paint particles in the paint booth and measurement of particle size distributions before and after the emission controls.

The study focused on aerosol sizes less than 15 μm. Two different coatings were used, a high-solids paint and an acrylic clearcoat paint as applied by three different industrial paint atomizers at varying atomization pressures. The results showed a particle size distribution that averaged 1 – 10 um with a Mass Median Aerodynamic Diameter (MMAD) of 6.6 um. Based upon this review of particle-size-distributions research, a method for collecting the particles of interest was needed, which is discussed next.

Paint overspray collection method

One critical factor for this effort was to physically collect a size distribution of primer overspray for further analysis. Methods available for the measurement of particle size distributions that don't physically collect the overspray are not applicable to this effort. There are numerous methods available to separate and collect particles based on size, such as inertial classification, gravitational sedimentation, centrifugation, and thermal precipitators. Inertial classifiers are the most common method of sampling for particles and include cascade impactors, virtual impactors, and cyclones (Marple et al, 1993: 203). A number of other sampling devices are available such as charcoal sorbent tubes (CSTs), diffusion monitors, and glass fiber filters. These media are primarily used for measurement of vapor mass and are not suitable for this effort.

Cascade impactors have been studied extensively, both theoretically and experimentally, and are the "instrument of choice" for the collection and determination of aerosol particle size distributions (Marple et al, 1993: 206) and were chosen as the sampling device for this effort.

Sampling Media

The choice of sampling media is important to the effectiveness of collection and analysis. If the media chemically reacts with the sample, compounds may be altered and the results may be biased. Most sampling and analysis methods for metallic elements require collection on cellulose ester filters (NIOSH Method 7082, 1994:1, NIOSH Method 7300, 1994:1, NIOSH Method 7024, 1994:1, OSHA ID-121, 1991:1). One OSHA method requires polyvinyl chloride (PVC) filters (OSHA ID-215, 1999; 1) for the collection of hexavalent chromium since interaction with cellulose filters resulted in up to 40% lower analysis results than the control due to possible conversion of Cr-VI to Cr-III (OSHA ID-103 Backup Report, 1991; 4). The NIOSH method for hexavalent chromium also calls for collection using PVC filters (NIOSH Method 7600, 1994: 1).

If a mixture of Cr-III and Cr-VI was expected in the samples of primer overspray, cellulose ester filters would bias the results in favor of Cr-III. For this study, the corrosion protection ingredients of the primers are all hexavalent chromium salts (Wallace, 1999) and it can be assumed that any chromium found in the analysis phase will have been in the hexavalent state when sampled. Background samples will also ensure that chromium was not inadvertently introduced to the samples. Therefore, cellulose filters were selected as the collection substrate because of their ability to be digested and the fact that chemical interactions were not a consideration.

Glass fiber filters are often used as the last collection surface of the cascade impactor. This filter offers excellent flow-through, prevents excessive pressure drop across the device and are less chemically reactive. Glass fiber filters were not selected based on the difficulty in digesting these filters in the analysis preparation phase.

Mixed Cellulose Ester filters were chosen as the collection substrate for this entire effort because they are chemically compatible for the purposes of our analysis and are completely digestible, eliminating the potential for residual solids that might reduce the chromium available for atomic absorption analysis.

The effective size of passageways through a sampling media (pore size) is important when compared to the expected size of the sample collected. If the pore size of a filter is too large, some of the sample will pass through the filter and bias the results. If the pore size is too small, airflow through the sampling device will be reduced and collection efficiency will decrease.

A pore size of 0.8 μm for the back-filter in the cascade impactor was selected based upon established sampling strategies (NISOH Method 7024, 1994:1, OSHA ID-121, 1991:7). The first six substrates in each cascade impactor are mounted on brass plates and do not have air flowing through them which eliminates the concern about pore size. The flow within the cascade impactor directs the aerosols of a particular size at the substrate, which is supported by the solid brass plate. The aerosols impact upon the substrate and collect on the surface. Cellulose filters with a pore size of 0.25 um were selected as the substrate for the impactors and will be referred to as substrates throughout the rest of this document except when referring to the back-filter in the cascade impactors which act as a filter through which air is drawn.

The collection surfaces mounted in the cascade impactor may be coated with greases or oils to provide a sticky surface on the impact plate and reduce particle bounce. These coating behave well on non-digestible materials such as stainless steel or aluminum substrates and can increase the collection efficiency of the impactor by approximately 10 percent. As the particles impact upon the coated surface, they stick and cover the coated substrate. To maintain the effectiveness of these coatings it is desirable to use a coating that has the capability of moving up through the deposited particles by capillary action to provide a continuous adhesive surface (Marple et al, 1993:215). Coatings will not be used in the effort in order to protect the integrity of the digestible cellulose substrates.

Sampling Location

Numerous exposure-related factors, such as multiple painters and the position of the painters with respect to the target, change the paint particle size distribution in the worker's breathing zone. To definitively characterize the exposure potential to painters, it is essential to collect samples from the breathing zone of the worker in an actual work setting. The objective of this research departs from the evaluation of breathing zone exposures in order to determine whether there is a chromium concentration bias in primer overspray particles of different sizes. Therefore, this effort will characterize the general overspray particle size distributions downstream of the painter and avoid the complications of replicating a breathing zone exposure.

Samples collected on a downstream test stand may not accurately simulate the complex airflows around a painter. This hypothesis has been challenged by at least one study that found no significant difference between test stand samples and personal samples (Brosseau, 1992).

Environmental Conditions

Environmental conditions are important in predicting the behavior of the primer overspray. Humidity can affect collected size distributions by reducing the potential for a particle to bounce off the substrate that it is supposed to collect on. Most atmospheric particles are hygroscopic and absorb more water as relative humidity increases. The pigment particles in paint attract moisture from the atmosphere. This retention of water has been shown to effectively eliminate the potential for fine atmospheric particles to bounce off the substrate when humidity levels above are 70% (Stein et al. 1994). The paint booth at the CTIO has the capability of maintaining a constant humidity level which can be used to reduce the potential for particle bounce by maintaining an elevated humidity. The effect of the absorption of any water will be eliminated by desiccating the filter before analysis.

Sample Evaporation and Preservation

A dynamic element of collecting aerosols generated by spray operations is the evaporative component of the airborne particle. Solvents in paint can consist of xylene, toluene, isocyanates, etc, and evaporation of these solvents will affect the size and mass of collected particles. Primers are designed to impact the surface of the target with sufficient solvents to effect polymerization of the paint matrix.

The temporal/spatial span during which evaporation of solvent in an airborne aerosol takes place can influence the impact location in a cascade impactor by reducing the particle's aerodynamic diameter, and the gravimetric analysis by reducing the mass of the particle collected. Samples taken during a study evaluating solvent exposures at an automotive plant with cascade impactors and in line Charcoal Sorbant Tubes (CST) showed no xylene on the impactor substrates following sampling. The conclusion proposed by this study was that either the particles were dry when collected or dried during sampling. No information was given on any solvent concentrations on the in line

CSTs (Cohen et al, 1992: 515), which may have indicated evaporation of solvent off of particles in the impactor.

One study performed a real time measurement of breathing zone particle sizes by measuring the footprint of particle impacts on a treated polycarbonate filter correlating the footprint to the expected spread of a given particle size (Carlton et al, 1997). This study effectively minimized evaporation bias experienced with other particle capture techniques following sampling, but does not address the potential for evaporation during flight. A comparison of evaporation during flight and following deposition in a sampling device would provide insight into the importance of post sampling evaporation as compared to evaporation during flight.

In order to avoid the complications of evaporative effects, this study will focus on the dry weight of the samples in order to create a consistent and reliable measure of the primer. Samples will be dried in a desiccator for at least 48 hours prior to gravimetric analysis.

Digestion Method

After collection, samples must be transformed into a physical state appropriate for spectrometry. This is accomplished by digesting the samples in acid. Two primary methods of digestion are hot plate digestion and microwave digestion. Research literature was reviewed in order to determine whether the hot plate or microwave method was the most effective way of preparing the samples. Considerations such as hazard level of chemicals involved and sample digestion time were important factors as well as the extraction efficiency of the method.

Two studies were found that directly compare hot plate digestion to microwave digestion. In the first study, USEPA method 3050 Hot Plate Method was compared with USEPA 3051 Microwave Method in the digestion of sediments and soils. The digestion time for the hot plate method was 90 minutes and involved the use of nitric acid and hydrogen peroxide. The digestion time for the microwave method was 10 minutes and called for the use of nitric acid only. The recovery efficiency for chromium using the microwave method was 38.7% compared to 22.8% for the hot plate method in one test, and 29.4% compared to 25.4% in a second experiment (O.I. Analytical, 1997).

The second study (Lachas et al, 1998: 180) compared microwave digestion and hot plate digestion for determination of trace elements in coal. The hot plate method involved sulfuric acid, perchloric acid, hydrofluoric acid, and nitric acid, while the microwave method involved only nitric acid. The hot plate method yielded 95% extraction of chromium compared to the microwave method that yielded 71%, leading to the conclusion that the stronger acids were necessary to break down inorganic bonds. No information was given regarding digestion times for either method in this study.

Recommended methods for sample preparation by nationally recognized organizations were investigated to determine the current recommended practice. One NIOSH method that addresses analysis of lead by AAS recommended a microwave digestion procedure for digesting paint (NIOSH Method 7082, 1994:5). Further investigation of NIOSH methods revealed a similar microwave method recommendation for analysis of various elements including chromium by Inductively Coupled Argon Plasma AAS (NIOSH Method 7300, 1994:1). Two NIOSH methods (NIOSH Method

7600, 1994: 1 and NIOSH Method 7024, 1994:1) both describe sample preparation processes for analysis of chromium using hot plate methods.

Several OSHA methods exist which address preparation of samples for similar analysis but each varies in one aspect or another from this effort. One method for analysis of hexavalent chromium using PVC filters requires a hot plate digestion method using perchloric acid which takes over 60 minutes per sample (OSHA ID-103, 1990:10). This method was superceded by a method designed to account for increased sensitivity requirements based on the proposed lower standard of .0005 mg/m^3 for strontium chromate. The new method (OSHA ID-215, 1998: 2) calls for collection of samples on PVC filters requiring use of perchloric acid in the hot plate digestion method. The method also includes steps using a solution of 5% NaOH + 7.5% Na_2CO_3 to assist in the extraction of strontium chromate from the solution. OSHA's general method for metals and metalloid particulates (OSHA ID-121, 1991:38) recommends a hot plate digestion process using HNO_3 and H_2O_2 for analysis of hexavalent chromium but also refers the reader to the OSHA specific process, OSHA ID-215, as a preferred method.

Both hot plate and microwave methods are recommended for reduction of the organic material in paints in different methods, but due to time and safety considerations and the lack of evidence supporting either method, microwave digestion was selected.

Particle Deposition

Particle deposition in the respiratory system is a critical factor in determining the health effects of the strontium chromate exposure. There are three primary regions of the respiratory system in which airborne particles can deposit upon exposure; the nasopharyngeal region, the tracheo-bronchial region, and the pulmonary region.

The nasopharyngeal region consists of the area from the nostrils to the larynx (Hughes, 1996:53) and filters out over 50% of particles larger than about 5 um and approximately 30 % of particles less than 1 um (Figure 3).

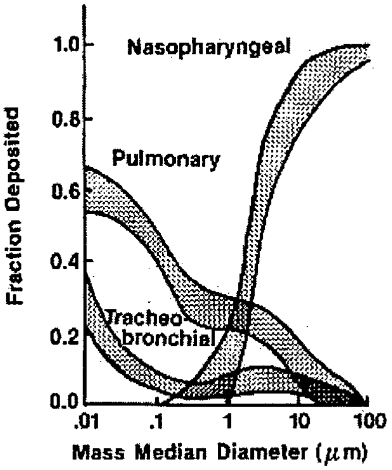


Figure 5.10 Deposition of particulate matter as a function of size[1]

Figure 3. Particle Respiratory Deposition (Godish, 1991:156)

The tracheo-bronchial region consists of the bronchi and bronchioles upon which particles that cannot navigate the bifurcations impact upon the bronchiole walls lined with mucus and cilia. These particles may be expelled from the lungs in a few days as a result of the mucociliary elevator action. This region has a high efficiency of collection for particles that are less than 0.1 um (Figure 4).

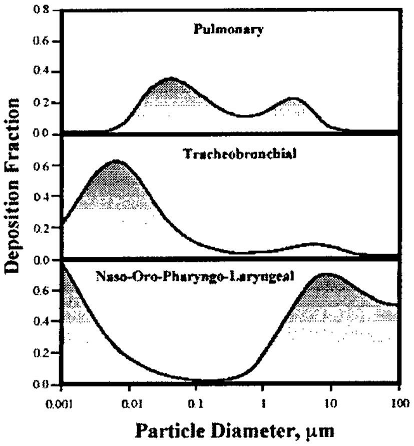


Figure 1.3 Fractional deposition in various regions of the respiratory system as a function of particle size for an average adult male. Adapted from NCRP, 1997.

Figure 4. Particle Respiratory Deposition (Health Effects Institute, 1998:2)

The pulmonary region consists of the terminal bronchioles and the alveoli where the exchange of CO_2 and O_2 take place (Fox, 1996: 175) and is the region where particles that settle out will most likely react with the body. Pulmonary deposition of particles is most efficient in the range of 0.01 to 2.5 um (Godish, 1991: 156).

The current ACGIH strontium chromate exposure standard is based upon the carcinogenicity of surgically implanted strontium chromate pellets in the bronchi of rat lungs (ACGIH TLV Documentation, 1998). This study may not take into account removal mechanisms such as mucociliary transport in the tracheo-bronchial region or impact in the nasopharyngeal region. Therefore, the exposure comparison to the standard may be more accurate if only the primer overspray that actually reaches the pulmonary region and is not expelled, (0.01 – 2.5 um) is evaluated. The expulsion of mucous into the digestive tract may cause adverse health effects that are beyond the scope of this effort.

Experimental Error

- Inaccurate weighing due to humidity effects on cellulose substrates during movement between the desiccator and microbalance

- Incomplete digestion of samples because of inadequate acid strengths during microwave digestion process.

- Volatilization of chromium during digestion and subsequent release during transfer form digestion vessels to sample bottles.

- Interference of compounds on chromium ions during AAS.

III. Methodology

Overview

This effort consisted of collecting aircraft primer overspray and analyzing the samples to determine chromium concentrations. Air sampling was performed in a paint booth using two seven-stage cascade impactors to obtain a particle size distribution of the overspray. A cartridge filter was also used to collect all particles as a quality control check on the total airborne concentration. These sampling devices were connected to a sampling train consisting of vacuum tubes that ran to a vacuum pump, flow meters, and pressure gauges. Samples were taken in an area downwind from the aircraft panel.

Following collection, analysis consisted of gravimetrically determining the particle size distribution for each sampling event using dry weight, digesting the samples by microwave digestion, and analyzing each particle size bin for chromium concentrations using AAS.

Equipment

Sampling Train

The sampling train was designed to sample primer overspray and to fit the configuration of the paint booth at the Coating Technology Integration Office (CTIO), Wright Patterson AFB, Ohio. Two seven-stage cascade impactors and one cartridge filter were driven by a GAST vacuum pump attached to a reservoir that smoothed out inherent fluctuations in flow from the vacuum pump (Figure 5 and Figure 6). ¼" Imperial Plastic vacuum tubing ran to Matheson rotometers which were used to control and monitor the flow volume through each sampling line.

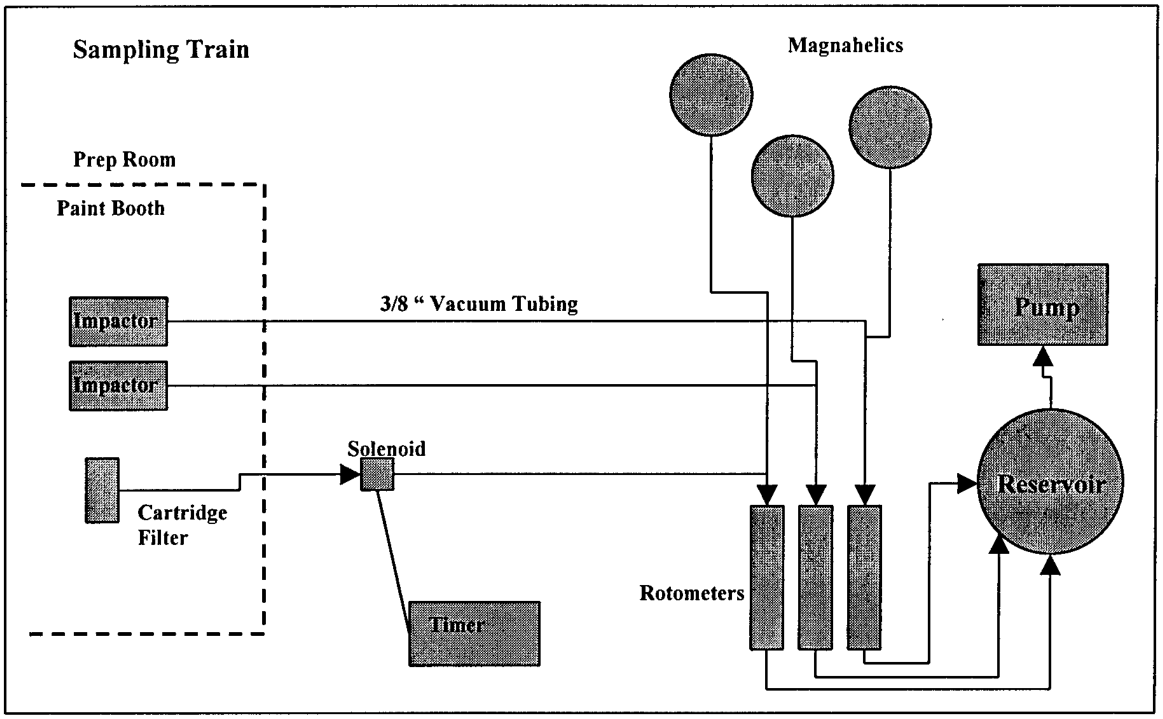


Figure 5. Sampling Train

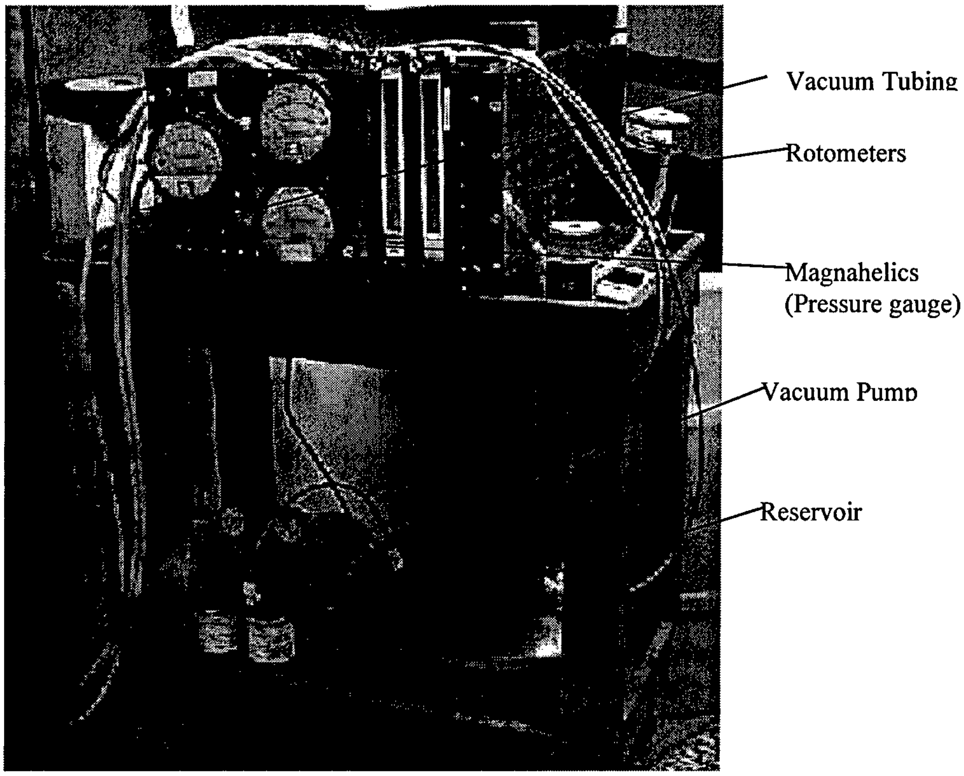


Figure 6. Sampling Equipment Outside Paint Booth

One 3/8" vacuum tube ran from the reservoir to the filter cartridge to determine the total mass concentration of chromium in the overspray. A Gralab electric timer was used to activate and deactivate a solenoid which controlled a valve to shut off flow through the cartridge filter. A Y-connector attached to the exit port of each rotometer provided connection to a Dwyer Instruments magnahelic displaying the pressure drop across each collection device (Figure 6).

Both the rotometers and the magnahelics were used as monitors of the performance for the cartridge filter and the cascade impactors. An excessive buildup of aerosol particles on a sampling device would affect both the flow of the air through the device and the accurate collection of material on the filters or substrates.

Cascade Impactor

A cascade impactor is an aerosol sampler for aerodynamic size distribution measurements of aerosols (Figure 7). Air is drawn through a series of progressively smaller round orifices on each of seven stages. The number of orifices on each stage increases with the decreasing diameter of the orifice (Table 2 and Table 3).

Figure 7. Cascade Impactor Assembly (PCSC, 2000)

The cascade impactor makes use of the fact that the Stokes number governs particle movement and impact through each stage. The Stokes number is a ratio of the stopping distance of a particle (a characteristic of the particle inertia) to the characteristic length scale of the flow, and will determine particle motion and whether particles impact on solid surfaces (Clark, 1996: 52). The aerosol is accelerated in each successive stage and particles too large to navigate the right-angle turns needed to continue through the impactor are collected on the plates holding the cellulose substrates. The increasing acceleration in each stage results in each successive collection surface (substrate) collecting a smaller particle size range (Figure 8).

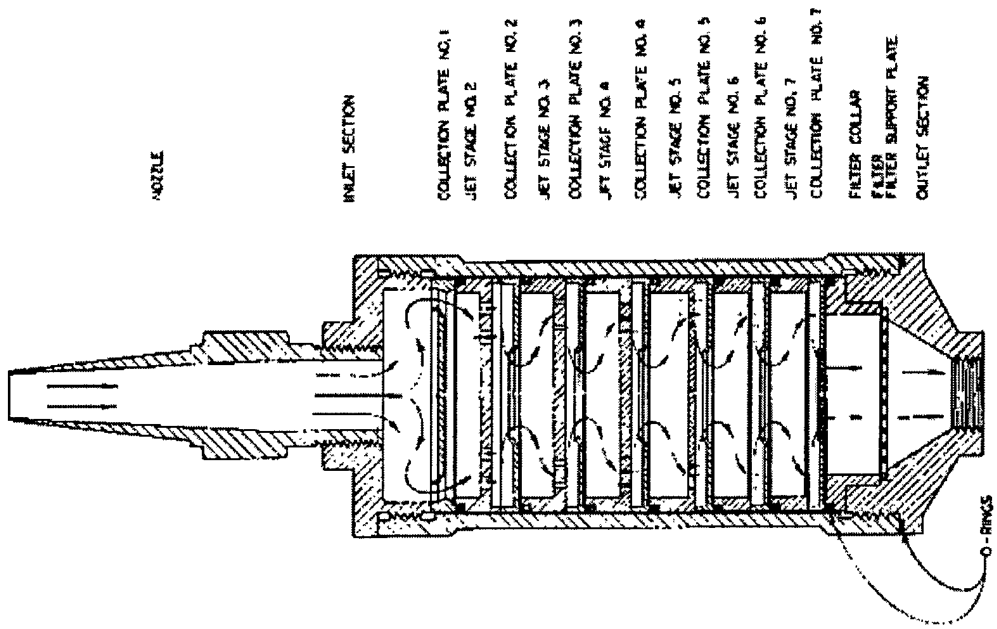


Figure 8. Flow Through a Cascade Impactor (PCSC, 2000)

The collection characteristics of the cascade impactor are a product of the design and quality of construction. A graph of the effective collection range of particle sizes for each stage gives insight into the effectiveness of the collection. The ideal impactor has a perfectly vertical efficiency curve. This would mean all particles larger than the cutoff size would collect on the plate while all smaller particles would pass on to the next stage. In reality the efficiency curves slope at either end of the plot (Figure 9) (Marple et al, 1993:211). From a practical standpoint, acceptable performance is that there will be no collection overlap between stages. If there is collection overlap, accurate quantification of the sampling results becomes difficult due to the inability to determine what percentage on each stage overlaps.

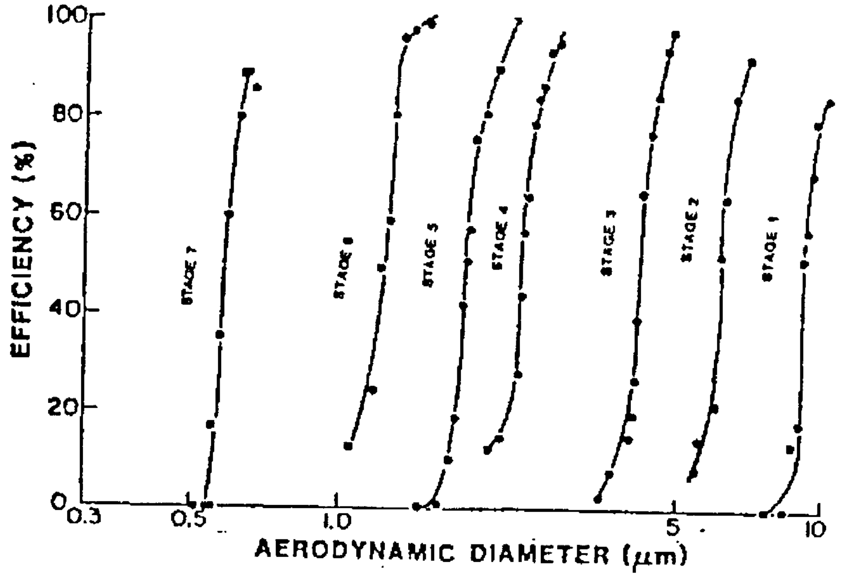


Figure 9. Cutoffs for Intox 7-Stage Cascade Impactor (Intox, 1995)

As a theoretical example, for a 2-stage impactor with cut-sizes of 10 and 5 µm, the first stage would collect particles larger than 10 µm, the second stage would collect particles between 10 and 5 µm, and particles less than 5 µm would be collected on the back-filter. A particle size distribution of the aerosol could then be determined by gravimetric techniques. Uncertainties in the particle size distribution of collected aerosols include the size of the largest particles collected on the first stage, and the size of particles collected on the back-filter (Marple et al, 1993:213).

The effective cutoff diameter for a stage is the aerodynamic diameter at which 50% of the particles impact on the collection surface (ECD 50%). The ECD 50% can be calculated for each stage by the following equation and the cutoff diameters for each impactor can be found in Table 2 and Table 3.

$$\text{ECD } 50\% = (.495\,(\mu)(D_j^3)(n)(\pi)/(Q)(\rho_q))^{1/2}$$

Where: 0. 495 = Stokes number for round jets (Hinds, 1982:118)
D_j^3 = Jet Diameter in cm^3
n = number of jets on the stage
$\pi = 3.1416$
Q = Volumetric flow in cm^3/sec = 10 lpm = 166.67 cm^3/sec
ρ_q = partial density for aerodynamic equivalent = 1 g/cm^3
μ = Viscosity of air at 70° F = 1.829×10^{-4} g/cm-sec

Table 2. Stage Information for In-Tox 7 Stage Cascade Impactor #1 @10 lpm

Stage	**1**	**2**	**3**	**4**	**5**	**6**	**7**
Number of holes per stage	1	2	3	4	6	9	12
Average Diameter (cm)	0.936	0.557	0.356	0.234	0.150	0.096	0.064
ECD 50% (10 lpm)	11.830	7.680	4.806	2.957	1.859	1.166	.733

Table 3. Stage Information for In-Tox 7 Stage Cascade Impactor #2 @ 5 lpm

Stage	**1**	**2**	**3**
Number of holes per stage	1	2	3
Average Diameter (cm)	0.936	0.557	0.356
ECD 50% (5 lpm)	16.730	10.861	6.797

Microwave Digestion System

O.I. Analytical's computer controlled microwave digestion system (Figure 10) consists of an acid-resistant oven exterior and an inner liner of molded Teflon that is acid resistant and microwave transparent. Software, combined with a pressure transducer, controls the pressure during the digestion process. The computer software automatically adjusts the power to the microwave to control the pressure. Real-time graphing and data acquisition allows for hard copy results of pressure parameters to assist in procedure development and data reporting.

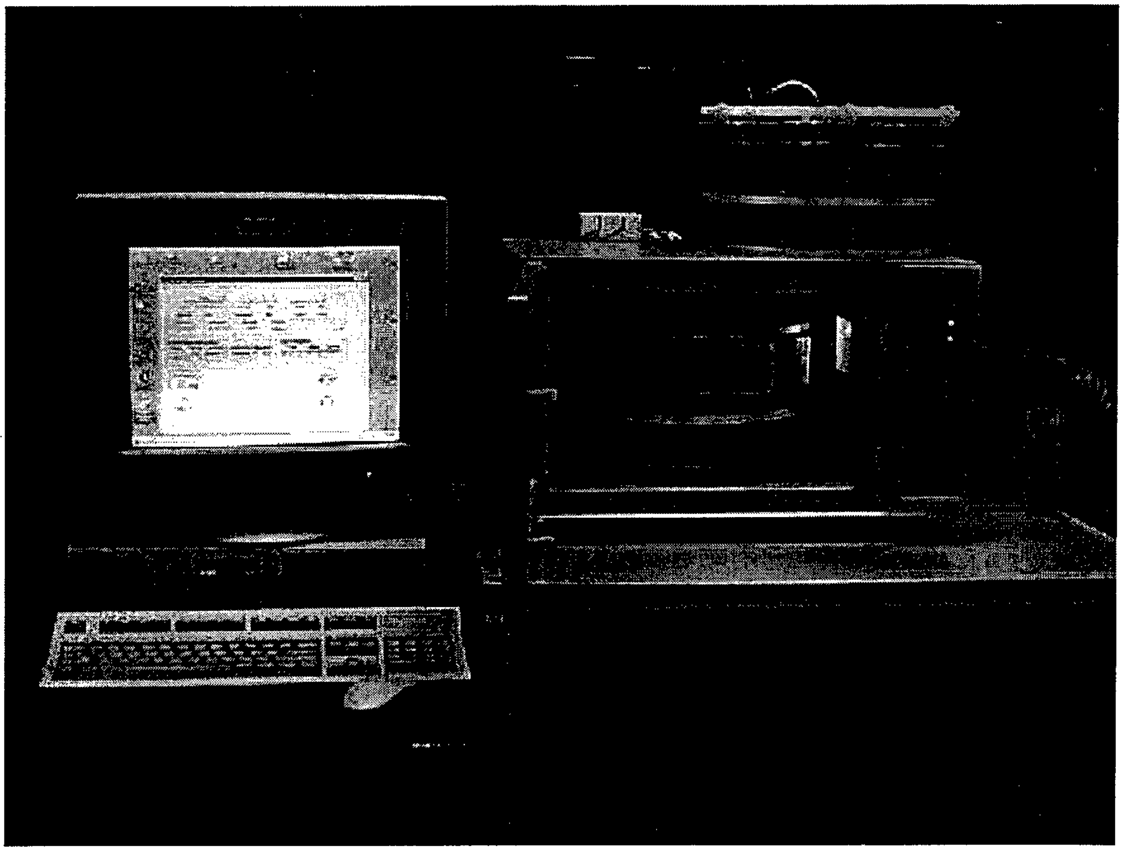


Figure 10. Microwave Digestion Unit

The system operates by using microwave energy to heat reagents and samples inside a pressurized, microwave-transparent digestion vessel. Pressurization of the vessels allows a higher temperature to be achieved, which increases the speed of digestion. Software controls the pressure inside a control vessel and the data is used to determine the amount of microwave energy applied.

Each sample is placed into one of 10 Teflon lined digestion vessels and then into a carousel that is loaded into the microwave unit (Figure 11). Each vessel is sealed with a Teflon cap containing a vent port that directs potential acid vapors to a central collection reservoir in case of over-pressurization. Each high-pressure digestion vessel is designed for up to 600 psi and 200° C.

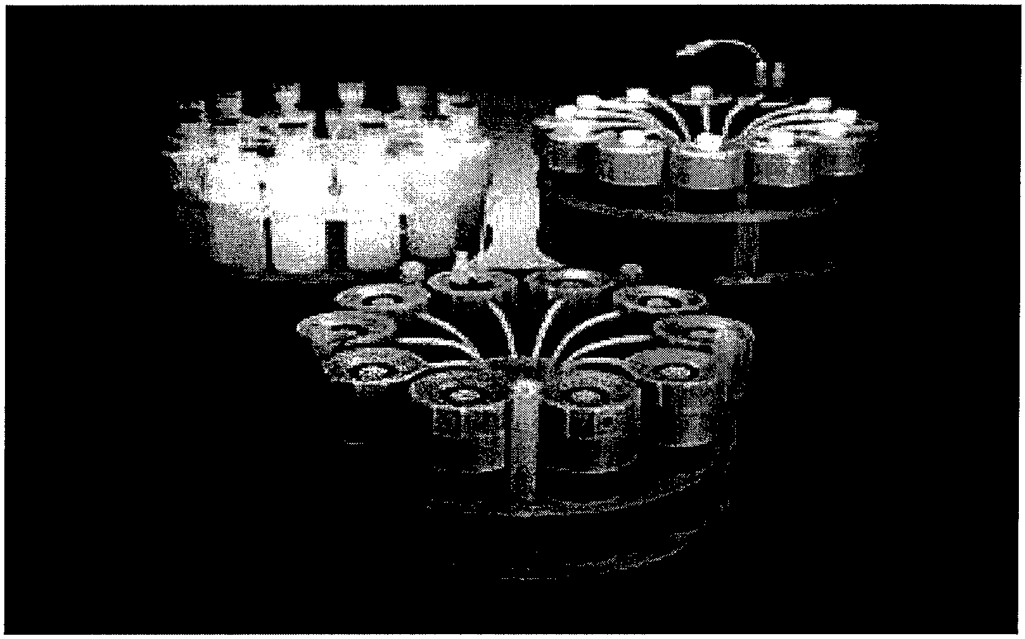


Figure 11. Microwave Vessel Carousel

Atomic Absorption Equipment

Chromium mass in the samples was quantified using a GBC Avanta atomic absorption spectrometer configured for air-acetylene flame measurement, or a graphite furnace configuration, depending on the expected mass of chromium in each sample (Figure 12). Atomic absorption spectroscopy is a measurement of the absorption of specific wavelengths of light by atoms using a flame atomizer, or graphite furnace, to atomize a solution containing chromium. The sample is drawn through a capillary tube into a nebulizer that converts the chromium solution and fuel into an aerosol that is forced into the spray chamber. Oversized droplets are drained out of the spray chamber and the resulting aerosol is fed into a laminar flow burner. The specific wavelength characteristic of chromium is isolated by a monochromator.

Figure 12. Atomic Absorption Spectrometer

Once the chromium/fuel mixture is ignited in the flame path, the flame will contain chromium atoms in the ground state since the temperature of the air-acetylene flame is not hot enough to excite them. These ground state atoms are able to absorb the narrow spectral line radiation emitted by applying a voltage to a hollow-cathode lamp with a chromium cathode.

As the photons pass through the flame, some possess just the right amount of energy (wavelength) and are absorbed by the chromium atoms. This absorption results in an excitation reaction, which raises an orbital electron to a higher shell level. AAS measures the difference in the amount of light emitted from the hollow-cathode lamp and the amount transmitted through the flame path containing chromium atoms (Beaty, 1993:1-3). This difference is the absorbance of the sample and is characterized by Beer's Law:

$$A = \text{Ln}\,(I_o / I_t) = a*b*c$$

where I_o is the initial intensity from the source, I_t is the transmitted intensity through the flame, A is absorbance, a is absorptivity, b is path-length (of the flame), and c is the concentration of analyte. Quantitative analysis results from comparison to a linear regression curve generated by using standards of known amounts of a specific compound or element in solution (Christian, 1994: 415).

Calculating an expected concentration of chromium for each sample prior to AAS helped determine whether flame or graphite furnace AAS was the best initial method. This was necessary because graphite furnace AAS has a much lower detection range than flame AAS, and samples with high chromium mass would saturate the graphite furnace and shorten the life of the furnace tubes. Conversely, running samples with very low chromium mass through the flame AAS would return concentrations well below the limit of detection. Both of these situations would cause excessive use of resources and increase the analysis time immensely by forcing repeat analysis of samples. Estimating chromium concentrations helped avoid these problems. Twenty milligrams of paint represented the upper limit of mass collected and provided a maximum expected chromium mass for calculation of expected concentrations.

$$\frac{1\ \text{sample}}{25\ \text{g soln}} * \frac{20\ \text{mg paint}}{\text{sample}} * \frac{0.19\ \text{mg SrCrO}_4}{1\ \text{mg paint}} * \frac{0.255\ \text{mg Cr}}{1\ \text{mg SrCrO}_4} * \frac{1000\ \text{ug}}{1\ \text{mg}}$$

$$= 38\ \text{ug/g (ppm)}$$

This provided a starting point by which dilution requirements could be pre-calculated based on the mass collected on each substrate. Samples that could not be diluted within the range of flame AAS (1 – 15 ppm) were stored until the spectrometer was re-configured for graphite furnace (10 – 70 ppb).

Primer Paint: Deft Primer – 02-Y-040

Deft primer 02-Y-040 was selected for this effort because of its heavy use in the Air Force. This primer meets the MIL-P-23377 military specification for an epoxy-polyamide, two part primer and provides excellent adhesion and hardness properties. It consists of a base component that contains the majority of the solids in the paint, and a catalyst containing primarily solvents (Table 4). The components are mixed in a 3:1 ratio (base:catalyst) and sit for 30 minutes prior to use. The remaining 38% of ingredients in component A are not hazardous and consists of various fillers and pigments that are not required to be listed on Material Safety Data Sheets (MSDS) by federal regulations.

Table 4. Deft 02-Y-040 Primer Components

Deft 02-Y-040 – Epoxy Polyamide		
Ingredient	Component %	Mixed Paint %
Component A (Base)		
Xylene	1	0.75%
Ethyl Benzene	1	0.75%
n-Butyl Acetate	5	3.75%
Methyl n-Propyl Ketone	25	18.75%
Strontium Chromate	25	18.75%
C8/C10 Aromatic Hydrocarbon	5	3.75%
Other Ingredients	38	28.50%

Component B (Catalyst)		
Polyamide Resin	50	12.50%
Aliphatic Amine	15	3.75%
sec-Butyl Alcohol	30	7.50%
C8/C10 Aromatic Hydrocarbon	2	0.50%
Amino Silane Ester	1	0.25%
Epoxy Resin Hardener	2	0.50%
Other Ingredients	0	0.00%

Procedure

1. Sampling:

The sampling phase of this experiment was conducted in a paint booth that is capable of maintaining constant humidity and temperature conditions at the Wright Patterson Air Force Base Coating Technology and Integration Office (Figure 13).

Figure 13. Environmental Control Paint Booth and Prep Rooms

The majority of the sampling train was located outside the actual paint booth in order to maintain an explosive safe painting environment (Figure 6). Three 3/8" vacuum hoses ran under the rubber door skirt to the sampling devices that were suspended at approximately four feet off the ground (Figure 14).

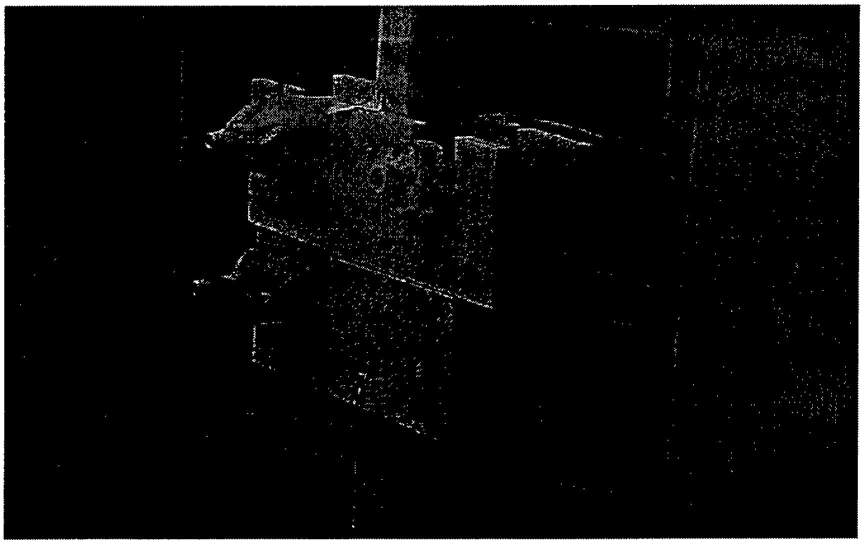


Figure 14. Air Sampling Equipment During Paint Collection

The painter mixed the paint, allowed for paint set-up according to manufacturer specifications, and applied the primer to various targets in a 180° orientation to the freestream flow through the booth (Figure 15). The airflow in the booth was 100 fpm as required by OSHA for painting operations. Standard Air Force safety and health equipment was used which included half-face air-purifying respirators, coveralls, and gloves.

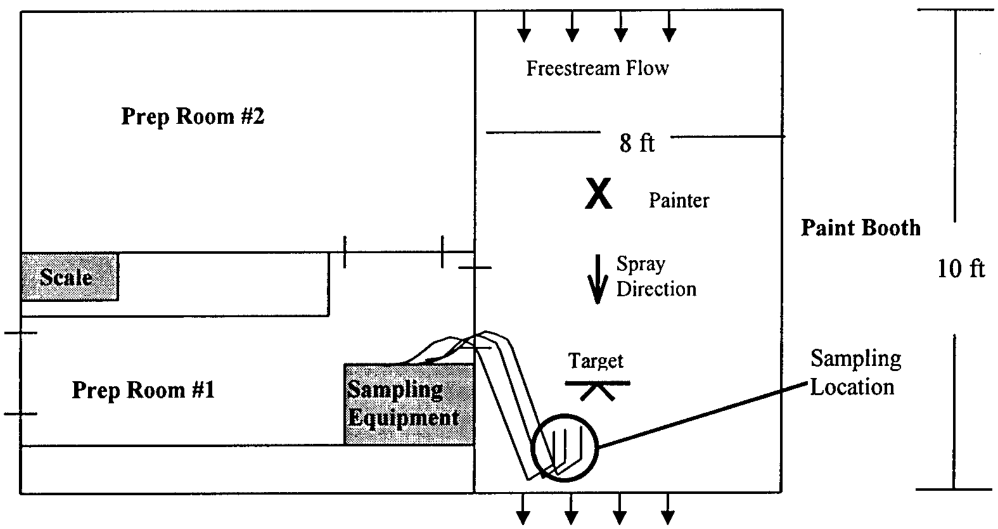


Figure 15. Paint Booth and Prep Rooms (not to scale)

The aircraft primer-overspray was collected using two cascade impactors and one cartridge filter located at the sampling location downstream from the target (Figure 15). The cascade impactors collected aerosol particles at a rate of 10 lpm and 5 lpm and the cartridge filter collected samples at 5 lpm.

Sample collection times ranged from 20 to 50 minutes depending on the length of the painting operation. Sample times were maximized to allow sufficient sample collection without overloading the substrates. The quantity of paint sprayed ranged between 800 and 1600 ml.

Once sampling was completed and the paint booth was clear, the cascade impactors and the filter cartridge were post-calibrated and then removed from the sampling lines. The cellulose substrates were removed from each sampling device with forceps, placed in an aluminum dish and stored in a desiccator for at least 48 hours. After drying, each substrate was weighed on an Ohaus model AP240 microbalance (Accuracy:

0.01 mg). After weighing, each sample was digested, analyzed, and stored in Teflon bottles according to the labeling scheme in Table 5.

Table 5. Sample Labeling Scheme

Date/Time:			
Carousel # - Vessel #	Filter location	Pre-weight	Post-weight
1 - 1	Stage 1 (25 mm)		
1 - 2	Stage 2 (25 mm)		
1 - 3	Stage 3 (25 mm)		
1 - 4	Stage 4 (25 mm)		
1 - 5	Stage 5 (25 mm)		
1 - 6	Stage 6 (25 mm)		
1 - 7	Back-Filter (47 mm)		
1 - 8	Cartridge Filter (47 mm)		
2 - 1	Stage 1 (25 mm)		
2 - 2	Stage 2 (25 mm)		
2 - 3	Stage 3 (25 mm)		
2 - 9	Cartridge Filter (47 mm)		

2. Digestion:

1. The O.I. Analytical microwave was calibrated to manufacture's specifications.

2. 5.0 ml of reagent-grade nitric acid was added to each vessel under a fume hood and capped.

3. Each carousel was irradiated to achieve a max pressure of 75 psi, with an initial stage of 50 psi. Power was applied for 25 minutes according to the Table 6 and Figure 16.

Table 6. Digestion Program for Epoxy Paint Chips with Nitric Acid

Stage	1	2	3
Power	90%	90%	0%
Pressure (psi)	50	75	0
Run Time, min	10:00	20:00	5:00
Time @ P, min	5:00	15:00	0:00
Temperature	~180° C	~180° C	Room Temperature

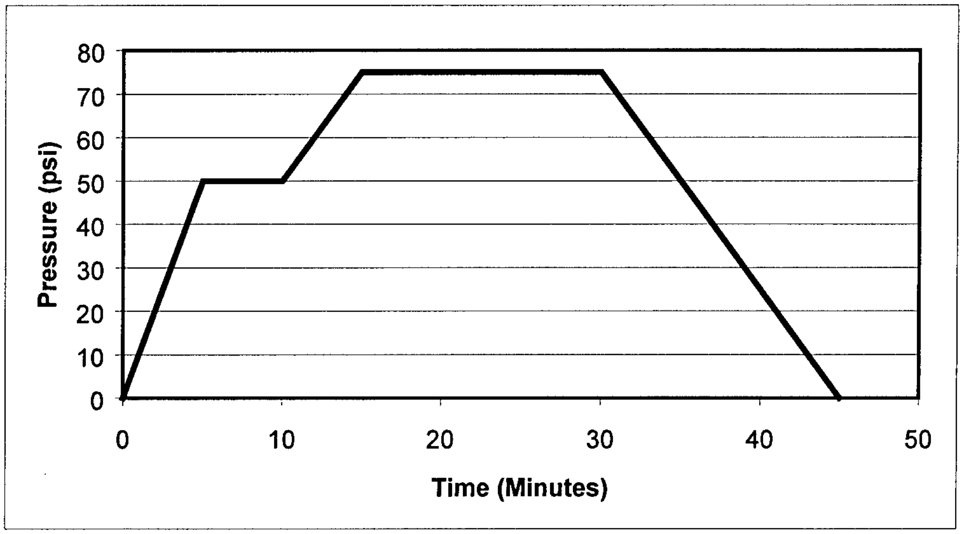


Figure 16. Digestion Program for Sample Preparation

4. The digestion vessels were placed in a bath of cool water to accelerate the cooling process.

5. Each digestion vessel was uncapped in a fume hood and 20 ml de-ionized water with 7% HNO_3 was added. The vessels were recapped, shaken thoroughly, transferred to 30 ml Teflon bottles, and sealed until analysis.

3. Flame AAS Analysis:

1. Samples above approximately 1 mg of total solid paint collected were analyzed by flame AAS. All other samples were analyzed using graphite furnace AAS.

2. The Avanta spectrometer was configured for Flame AAS and samples identified for flame analysis were loaded into test tubes designed for the auto sampler.

3. Four standards (1, 5, 10, and 15 ppm) were prepared from a certified 1000 ug/ml source of hexavalent chromium and a calibration curve was created by following Avanta procedures. The software was set to fail the calibration process at a R^2 value less than 0.980.

4. Three replicates were performed for each sample. The auto sampler drew the sample through a capillary tube that was rinsed between samples. A check sample of 10 ppm was run at the end of the each series of 10 to 15 samples to check for a shift in the calibration curve during the run. A sample blank was analyzed after the calibration curve was generated.

5. Samples that were measured at absorbance values outside the calibration curve were diluted and re-analyzed.

4. Graphite AAS Analysis (For samples 0 - ~1 mg):

1. The Avanta spectrometer was configured for graphite furnace by removing the flame burner and attaching the furnace assembly (Figure 17).

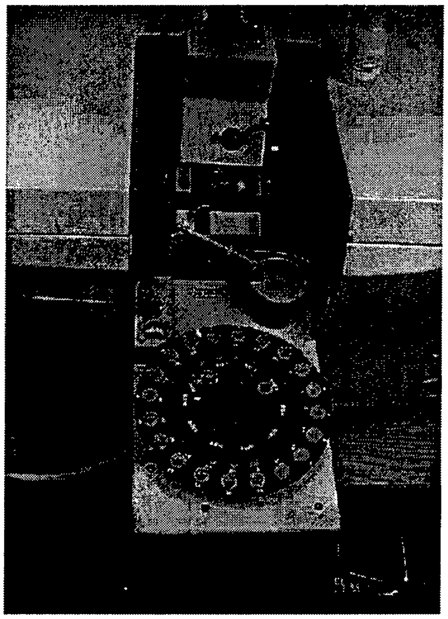


Figure 17. Graphite Furnace Assembly with Auto Sampler

2. A calibration curve was made using a GBC auto-mix feature that produced a 5-point calibration curve (10, 25, 40, 55, 70 ppb). The software was pre-set to fail if the R^2 value of the calibration curve was less than 0.980.

3. A certified check standard of 20 ppb was included at the end of each run of 5-15 samples, and also in the middle of the run if the number of samples was over 15.

4. Three replicate measurements were made for each sample. Each of the three replicates for a given sample was measured in series but in a discrete manner (Data on the graphite furnace configuration can be found in Appendix C).

5. An auto-dilution feature was used to dilute samples that were above the highest point of the calibration curve. Samples that failed the initial measurement were diluted by 80%, and could be diluted by 90% before the system failed the sample measurement.

IV. Results and Analysis

Overspray Distributions

Impactor #1 gave a collection range between 11.8 um and 0.7 um at a flow rate of 10 lpm. We expanded the upper range of our effective particle size collection by loading the top three stages of an identical impactor and collecting in parallel with impactor #1 at a flow rate of 5 lpm. This reduction in flow allowed us to collect particles above 16.7 um, 10.8 um and 6.7 um. These additional bins (6.7 – 10.8 um, 10.8-16.7 um, and >16.7 um) were used in the determination of chromium concentrations in addition to the bins from impactor #1 but were not used in the generation of a particle size distribution.

92% of the paint mass collected in impactor #1 (and 80% of the mass collected in impactor #2) was deposited on the top stage of the impactor (Table 7). These results parallel an earlier study that found 80% of aerosol deposition on the upper stage of a 4-stage cascade impactor with a 7 um top-stage cutpoint (Brosseau 1992). The differences between these two studies are most likely due to many situational factors such as variable sampling locations, ventilation systems, paint viscosity, spray equipment, and paint ingredients.

The heavy loading of paint particles on the first stage indicated that the distribution of concern to this effort was a small part of a much larger distribution. Based on this information, the top stages were considered a pre-cut filter and stages 2-7 were used to calculate the particle size distribution. Particles greater than 11.8 um in size were not included as data in the process of generating the distribution but were used in the determination of chromium concentrations.

Table 7. Collection Results of Impactors #1 & 2 (in ug)

Impactor #1	ECD(50%) um	14 Oct PM	21 Oct AM	21 Oct PM	22 Oct AM	22 Oct PM	29 Oct AM	2 Nov AM
			ug of	paint	collected			
1	>11.8 um	12870	34640	27530	19650	24230	28640	6660
%		89.3%	94.0%	92.7%	92.3%	91.9%	89.2%	93.8%
2	7.7 um	650	970	850	890	770	1350	160
3	4.8 um	430	610	640	450	480	780	60
4	2.9 um	230	340	280	30	290	460	0
5	1.8 um	100	100	130	100	180	340	120
6	1.1 um	40	130	160	80	140	140	0
7	0.7 um	20	50	0	30	100	0	0
Back-Filter	<.7 um	80	0	100	50	170	387	100
Impactor #2	ECD (50%) um	14 Oct PM	21 Oct AM	21 Oct PM	22 Oct AM	22 Oct PM	29 Oct AM	2 Nov AM
1	> 16.7 um	4160	11220	9660	6320	9270	8010	2520
%		78.0%	83.0%	82.4%	81.3%	85.0%	76.8%	79.7%
2	10.8 um	840	1570	1500	1180	1140	1620	440
3	6.7 um	330	720	570	270	490	800	200

The distributions of the samples with cutpoints less than 11.8 um are shown in Figure 18. The Mass Median Aerodynamic Diameter (MMAD) was 6.0 um, and the Geometric Standard Deviation (GSD) was 3.03 um.

The MMAD is a descriptive parameter of a distribution that is based on the mass collected and represents the size at which 50% of the mass collected is above this value, and 50% is below this value. There are other descriptive parameters that can be used such as Geometric Mean Aerodynamic Diameter, which is based on size characteristics such as volume or surface area and Count Median Diameter that is based on a numerical count of particles. The Geometric Standard deviation is a measure of the spread of the data.

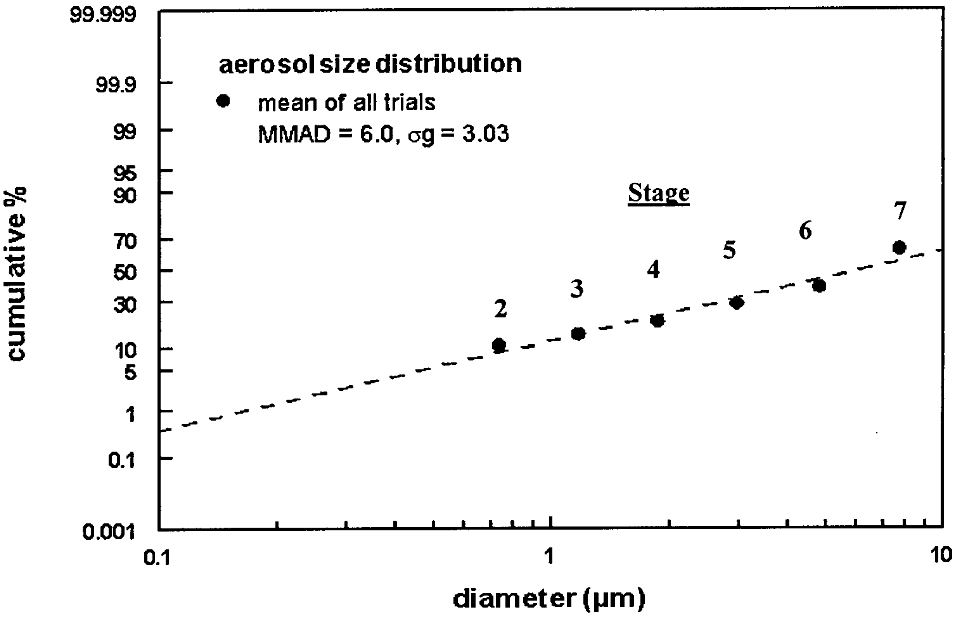


Figure 18. Impactor #1 Distribution (Stages 2 - 7)

Chromium Analysis

The digested samples were analyzed by either Flame AAS or Graphite Furnace AAS. Figure 19 shows the resulting concentrations for each particle size bin of the two impactors. Each value on the graph is the concentration of chromium mass per mass of total solid paint collected and is an average of 10 separate sampling measurements. Tabular results can be found in Appendix A.

It is important to note that the concentration value for each cutoff diameter indicates the concentration for particles between that cutoff diameter and the next largest cutoff diameter.

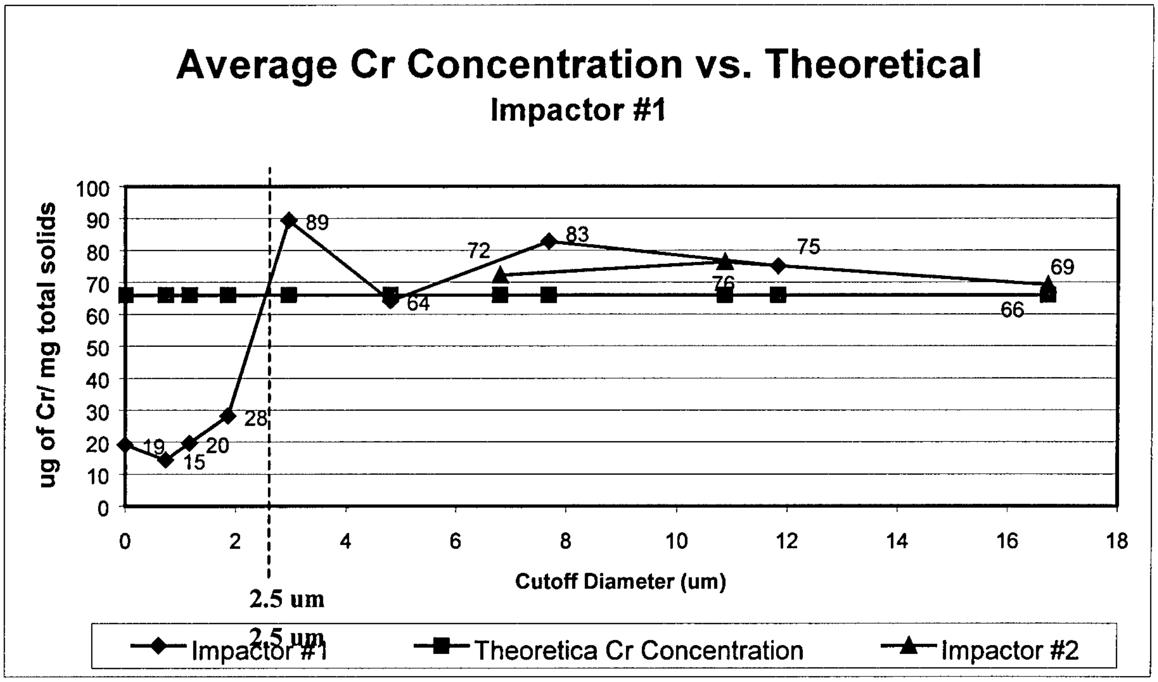


Figure 19. Average Chromium Concentration

Visual evaluation of the average chromium distribution (Figure 19) indicated a possible difference between the concentrations for particle sizes less than 2.5 um and for particle sizes greater than 2.5 um. This apparent separation split the data into two groups which are referred to throughout the analysis and discussion.

The Material Safety Data sheets for Deft Primer 02-Y-040 gives the solid to volatile ratios for both components of the primer, which allowed for calculation of the theoretical strontium chromate concentration (66 ug/mg) as compared to the solid fraction of the primer. This calculation assumes the particles to have the same chemical composition as the paint itself. Figure 19 shows the analysis results of this sampling effort with the theoretical concentration of the primer based on the MSDS information. Table 8 shows the calculation of the theoretical concentration.

Table 8. Theoretical Chromium Concentration Calculation

Calculation of Theoretical Concentration (Chromium mass vs Total solid mass)		
Component	A	B
Total mass of each component (mg)	1200	400
% SrCrO4	0.25	0
SrCrO4 mass (mg)	300	0
% Cr (in SrCrO4)	0.255	
Cr Mass (ug)	76500	
% Solid	0.72	0.7
Total Solid Mass (mg)	864	280
Total Solid Mass (A & B)	1144	
Cr Concentration (ug/mg)	**66**	

The standard deviations for individual measurements for the top stage of each impactor were consistent ($\sigma = 3 - 14$) compared to the other stages. The intermediate stages (7.6 um - 2.9 um) are much more variable ($\sigma = 30 - 96$). This may be due to the highly variable characteristics of the particles at these stages or may reflect error introduced by smaller samples. The lower stages (1.8 um - .7 um) had a tighter distribution than the intermediate stages ($\sigma = 9 - 19$).

There were some notable outliers in the data (Appendix A). The most significant outlier was a value of 331 ug chromium /mg paint in the 2.9 um bin, which was 5 times the average of the other data points in the same bin (Table 9.a.), and caused the 2.9 um bin to exhibit attributes of both the higher and lower concentration groups identified during visual evaluation of the concentration graph (Figure 19). This raised the question as to which group the 2.9 um bin belonged or if it was significantly different from both groups.

Further evaluation of the 2.9 um bin data showed that the statistical summary information corresponded more closely to the higher concentration group (Table 9 a.), but numerous concentration values (Table 9 b.) fell in the range of the lower concentration grouping. Determination of the appropriate concentration grouping for the 2.9 um bin was conducted along with the statistical test to determine if there was a statistically significant difference between the two apparent concentration groupings.

Table 9. 2.9 um Cutpoint Particle Data

a.

Statistical Summary (2.9 um)	
Mean	89.398
Median	50.438
Standard Deviation	96.544
Range	303.115
Minimum	28.197
Maximum	331.312

b.

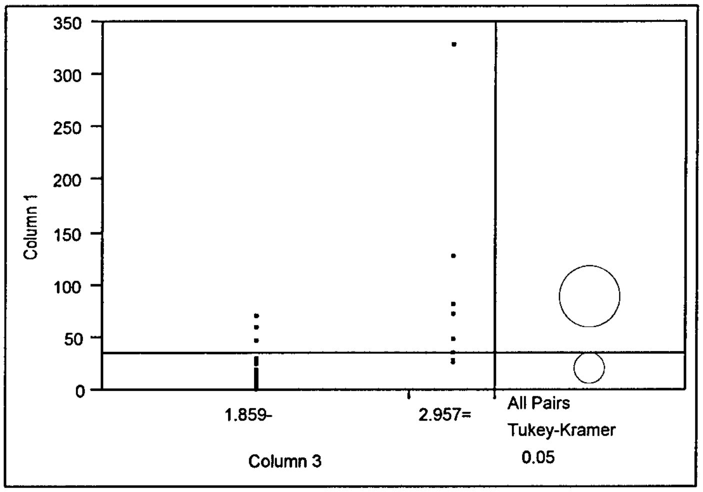
Sample Date	*Concentration Value (2.9 um)*
18 Nov 99 AM	130.440
14 Dec 99 AM	75.281
16 Dec 99 AM	37.549
14 Oct 99 PM	30.562
21 Oct 99 AM	50.438
21 Oct 99 PM	83.481
22 Oct 99 AM	331.312
22 Oct 99 PM	37.322
29 Oct 99 AM	28.197

Statistical Analysis

A Wilcoxin Ranked Sum Test was used to determine to which group the 2.9 um cutpoint samples belonged or if it belonged in its own group. A second ranked sum test was performed to determine whether or not there was a significant difference between the different concentration groupings. The Analysis of Variance test to determine a difference between means of two populations is a robust test that was considered for use, however, key assumptions underlying the test were not met. The distribution of the data could not be assumed to be normal and the variances of the data sets were very different, so the Wilcoxin nonparametric test was chosen to evaluate the data (Devore, 1995: 207). The SAS JUMP statistical software package was used to perform these tests.

Three groups were identified for evaluation. The first was the lower concentration group (< 2.9 um). The second was the 2.9 um concentration group which showed the potential of belonging to either the higher concentration group or its own group. The third was the high concentration group (>2.9 um). These three groups were analyzed against each other for significant differences.

The results of the lower concentration group comparison with the 2.9 um concentration group showed a statistically significant difference (P-value <0.0001) and is graphically represented by non-overlapping comparative circles (Figure 20), which vary in size according to the data set's variance. The axis-labels on the graph are show the columns of each data set in the software package. This indicated that the 2.9 um cutpoint group was significantly different from the small group. The next step was to determine if the 2.9 um cutpoint group was its own group or if it belonged to the high concentration group.



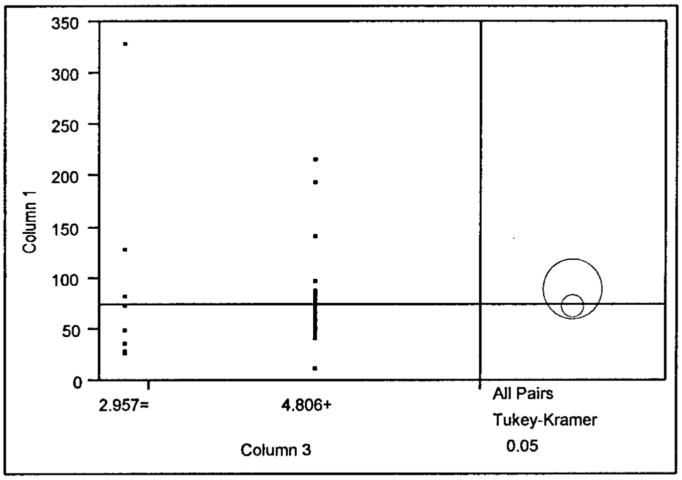
```
Wilcoxon / Kruskal-Wallis Tests (Rank Sums)
 Level   Count Score Sum Score Mean(Mean-Mean0)/Std0
 1.859-     33       585    17.7273          -3.801
 2.957=      9       318    35.3333           3.801

 2-Sample Test, Normal Approximation
                    S        ZProb>|Z|
                  318  3.80102  0.0001

             1-way Test, Chi-Square Approximation
             ChiSquare     DFProb>ChiSq
               14.5645      1    0.0001
```

Figure 20. Wilcoxin Ranked Sum Test Results (< 2.9 um vs. 2.9 um)

The results of the large cutpoint group comparison with the 2.9 um cutpoint group did not show a statistically significant difference (P-value = 0.4418) and is graphically represented in Figure 21. This indicated that the 2.9 um cutpoint group could not be shown to be different from the large cutpoint group. Based upon these results, the 2.9 um cutpoint group was combined with the larger concentration group for the purpose of further evaluation.



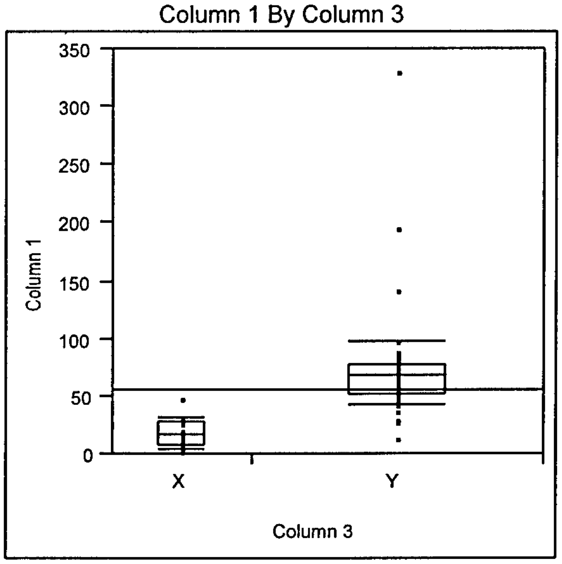
```
Wilcoxon / Kruskal-Wallis Tests (Rank Sums)
 Level   Count Score Sum Score Mean (Mean-Mean0)/Std0
 2.957=      9       268    29.7778           -0.760
 4.806+     59      2078    35.2203            0.760

 2-Sample Test, Normal Approximation
                  S        ZProb>|Z|
                268 -0.76010  0.4472

            1-way Test, Chi-Square Approximation
            ChiSquare     DFProb>ChiSq
               0.5916      1     0.4418
```

Figure 21. Wilcoxin Ranked Sum Test Results (2.9 um vs. > 2.9 um)

The Ranked Sum test was performed again with two concentration groups (Figure 22). There was a statistically significant difference (P-value < .0001) between the means of the two concentration groupings. This indicates that there is a significantly larger concentration of chromium in paint overspray particles 2.9 um or greater than in particles smaller than 2.9 um.



```
Wilcoxon / Kruskal-Wallis Tests (Rank Sums)
  Level  Count Score Sum Score Mean(Mean-Mean0)/Std0
  X         23      309   13.4348            -6.340
  Y         47     2176   46.2979             6.340

  2-Sample Test, Normal Approximation
                       S       ZProb>|Z|
                     309 -6.33952  <.0001

                 1-way Test, Chi-Square Approximation

                 ChiSquare     DFProb>ChiSq
                   40.2689      1    <.0001
```

Figure 22. Two Way Wilcoxin Ranked Sum Test Results

Sample Loss

The 22 Oct PM set of samples (See Appendix A for raw data) experienced potential sample loss when the pressure transducer monitor sprung a leak and full power was applied throughout the digestion program instead of cycling the power on and off based on the pressure readings of the control vessel. This caused the safety pressure seals on the digestion vessels in carousel #2 to burst releasing vapors into the overflow container. These four digestion vessels had no liquid remaining after the run and were rinsed with 25 ml of de-ionized water instead of the 20 ml for normal samples to maintain the 25 ml end volume desired. The results of AAS were very close to the values for unaffected samples but it cannot be determined if the loss of chromium was low or if the samples were significantly higher in concentration and a large amount was lost. Since the end result of analysis was consistent with the expected results and other comparable samples, the data was included in the results.

Several samples were taken throughout this effort that resulted in zero mass being collected on the substrates after desiccation. Theoretically, there should have been no chromium on these substrates upon analysis by AAS. Table 10 shows one sample from the 16 Dec sampling event and several control samples that were taken in the paint booth with no on-going paint operations.

Table 10. Resulting Chromium Concentration (zero mass collected)

Date	ID	Pre - Weight (g)	Dry - Weight (g)	Mass Collected (mg)	Calculated Cr (ppb)	Cr Concentration (ug/mg)	Cutoff Size (um)
16 Dec 99	1-6	0.059	0.059	0.000	.043132	N/A	1.166
Control	1-3	0.065	0.065	0.000	.012238	N/A	4.806
Control	1-4	0.065	0.065	0.000	.011583	N/A	2.957
Control	1-5	0.064	0.064	0.000	.011761	N/A	1.859
Control	1-6	0.064	0.064	0.000	.011437	N/A	1.166
Control	2-3	0.066	0.066	0.000	.012201	N/A	6.797

The results showed no increase in substrate mass in post sampling gravimetric analysis but resulted in measurable concentrations of chromium in the analysis. One likely explanation would be contamination in the analysis process but the measured concentrations are fairly consistent across the samples at approximately 12 parts per billion, which is close to the detection limit of the graphite furnace configuration. This would indicate that the readings are a result of random error in the analysis process that cannot be controlled but can be accounted for in the results.

The consistent measurement of 12 ppb in zero mass samples hints at a process wide bias that might result in an overstatement of all sample concentrations. Another explanation for a measurement of zero mass on the substrates could be errors in the weighing process. Fluctuations in humidity during the weighing process could affect the difference in pre and post sample weights. If the pre-sample substrate was exposed for sufficient time to collect atmospheric water, then upon post-sampling dessication, this additional weight might have been driven off resulting in no mass increase when paint mass had actually been collected.

A consistent bias of 12 ppb across all results would not affect the conclusion that there is a significant difference between the two concentration groupings of dry mass.

V. Discussion

The difference in the concentration of chromium between the two groupings could be a result of many factors. One possible explanation could be related to the particle size of the strontium chromate as an ingredient of the primer. The strontium chromate used in the Deft 02-Y-040 primer that was sampled during this effort is received from an outside supplier and has a particle size distribution between .2 um and 10 um when mixed into the primer (Figure 23). The distribution is measured as a suspension of strontium chromate in a liquid and represents the most complete separation of strontium chromate particles that could be expected from the source. The strontium chromate comes to Deft in a powder form and agglomerates either prior to addition to the paint mixture or after.

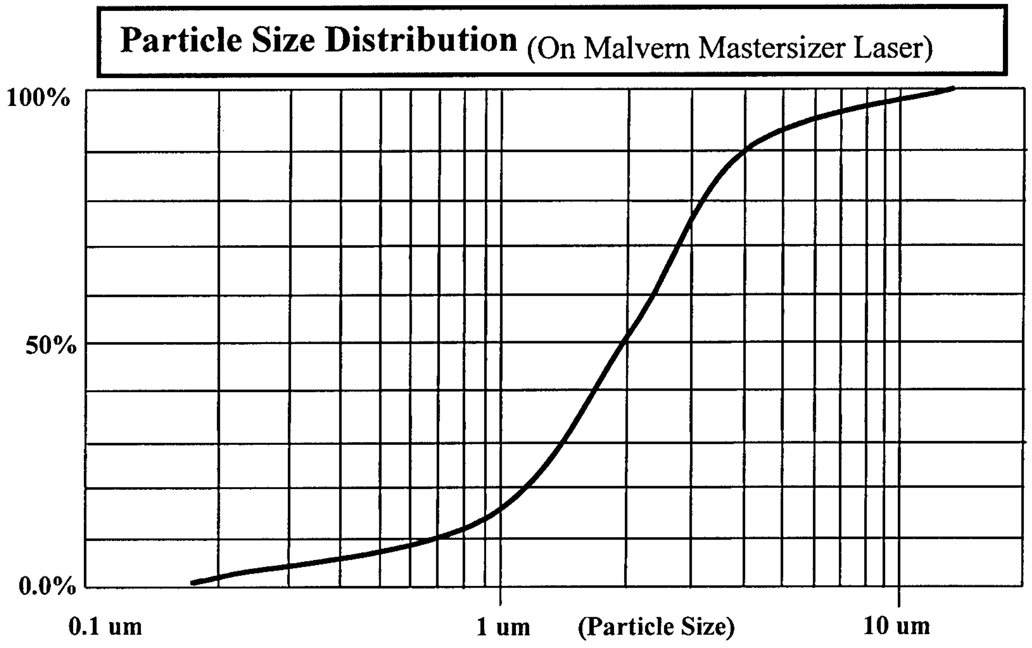


Figure 23. Strontium Chromate Particle Size Distribution

The agglomeration of the strontium chromate particles to the other primer ingredients including solvents, fillers, pigments, and resins will form the paint as it is mixed. As paint exits the spray gun, the spray droplet may consist of a nucleus of strontium chromate with a coating of solvents and other ingredients. This liquid coating could form a coating of uniform thickness around the strontium chromate nucleus. The larger the strontium chromate particle, the larger the ratio of chromate to all other ingredients. It is expected that the larger droplets will have a larger concentration of chromium for this reason.

Another possible influence on chromium concentrations is that during flight, turbulence may strip smaller droplets of solvents off the paint droplet (Figure 24) that will consist of primarily the volatile portion of the paint. The majority of these volatile droplets would fall below the 2.9 um cutpoint and create the lower or zero concentrations in the smaller particle size bins.

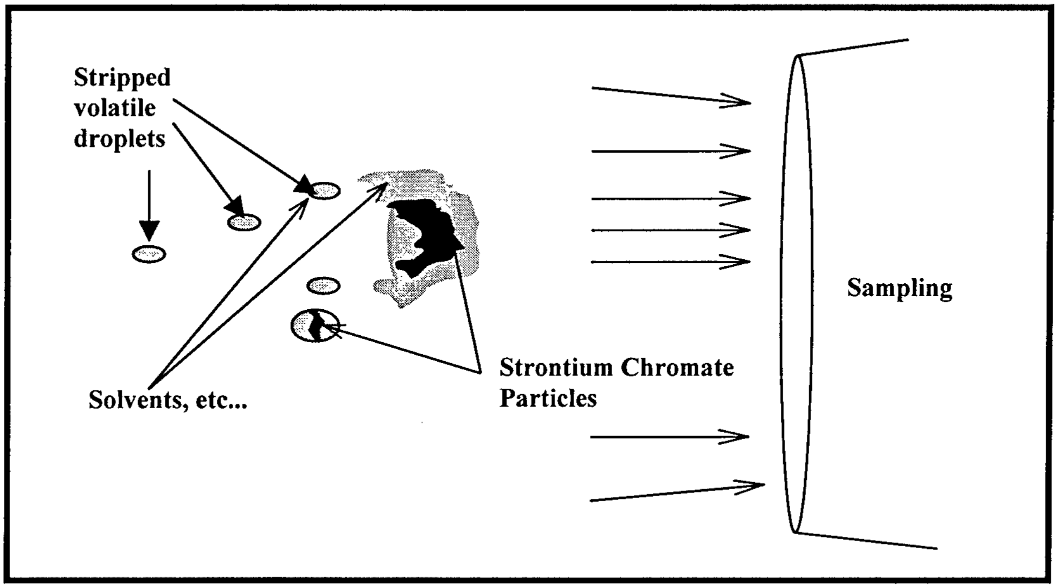


Figure 24. Primer Droplet separation

The remaining large droplets with a large strontium chromate nucleus would fall primarily above the 2.9 um cutpoint and fall into the larger concentration grouping. Some of the droplets from the spray gun will have sufficient mass stripped during ejection from the nozzle, or during flight, that small chromate particles with little or no solvent attached could be smaller than the 2.9 um cutpoint. These would deposit in the lower concentration grouping and could account for there not being a total absence of strontium chromate at the small particle sizes.

Another possible factor explaining the concentration difference might be the liquid to solid ratio differences between the small particles (<2.5 um) and large particles (>2.5 um) prior to impacting on the cellulose substrates. The analysis of the samples was based on a dry weight measurement after collection in order to minimize the variation caused by different drying times for different masses of sample collected. Assuming an equal ratio of the paint ingredients for both small and large particles (Figure 25), the concentration of chromium would remain constant as the liquid portion of the primer evaporated.

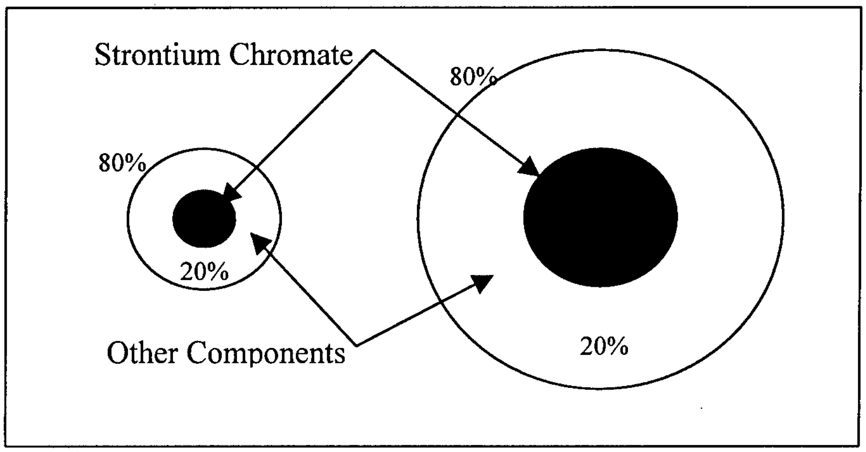


Figure 25. Homogeneous Sr(CrO4)/ Solvent Mixture

However if the ratio of strontium chromate to other ingredients were smaller in the small particles, which might be expected if a coating of uniform thickness surrounds both small and large chromate nuclei alike (Figure 26), the drying process would cause a relative increase in the dry mass concentration of chromium.

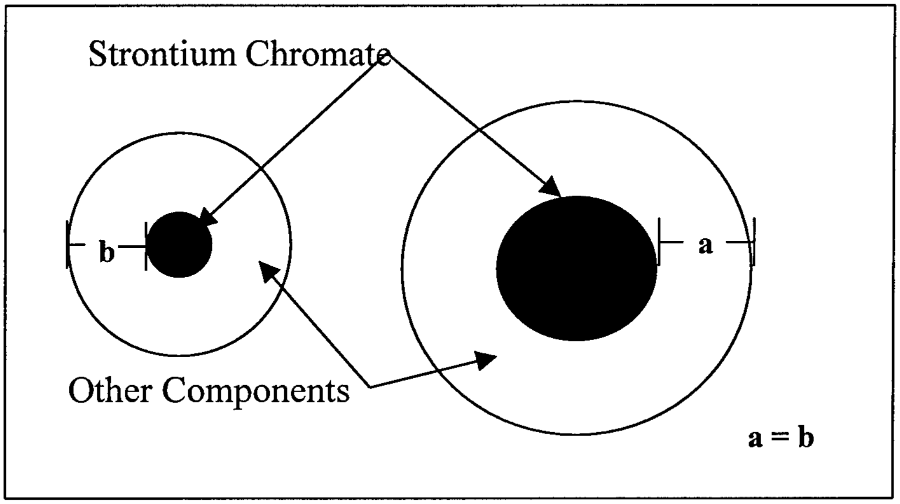


Figure 26. Heterogeneous Sr(CrO$_4$)/ Solvent Mixture

Given a heterogeneous mixture, the concentration of chromium in small particles may be over reported in dry weight analysis measurements and the results of this thesis effort may be conservative by understating the actual difference between small and large particle concentrations.

Another way to evaluate the results of this thesis is to compare the mass of chromium collected for each cutpoint to only the total chromium collected in each impactor (Figure 28). This eliminates the effects of solvent evaporation and heterogeneous paint mixtures on a concentration value, and allows for comparison of the chromium mass deposited by cutpoint size. Figure 27 shows that 86% of the overspray collected falls above 11 um, and 77% falls above 16.7 um. Less than 6% of the chromium mass collected was bound in particles less than 3 um. Again, it is important to note that this distribution is not representative of a breathing zone sample taken in an actual working environment.

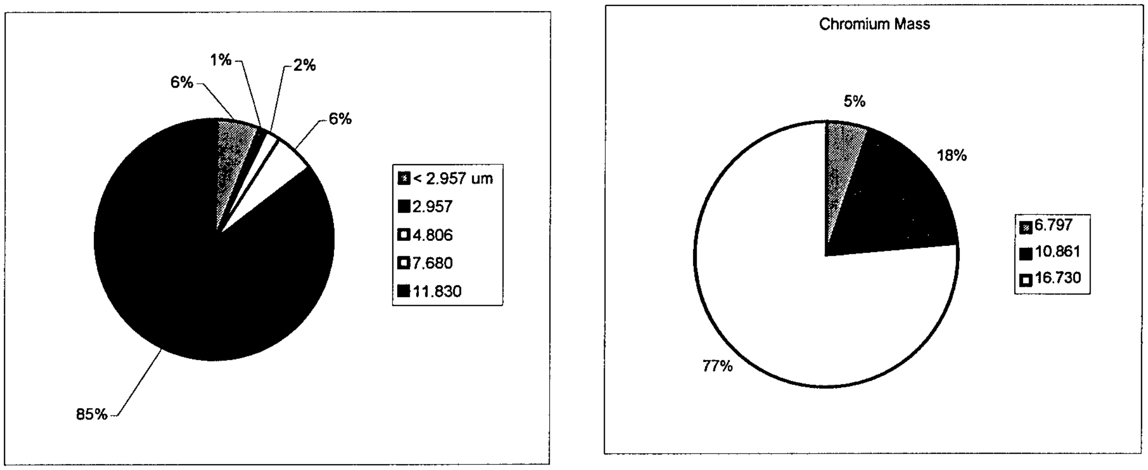


Figure 27. Percent of Chromium Mass per Total Chromium Collected: Cascade Impactor #1 and #2

Implications

Industrial hygiene personnel perform theoretical calculations in lieu of sampling, or as a precursor to sampling, for industrial operations. Figure 19 shows that theoretical calculations based upon MSDS information and paint usage will overstate the actual exposures by up to 3 times. This practice may result in the use of protective equipment beyond what is necessary for adequate worker protection or regulation in excess of necessary levels.

The results of this study provide evidence that the concentration and mass of chromium deposited in the pulmonary region of the lungs may be significantly less than what is deposited in the upper regions. If the upper respiratory system eliminates foreign matter in a faster and more efficient manner than the pulmonary region, then this study shows that pulmonary dosing is less of an exposure hazard than would be concluded by assuming an equal distribution of chromium across all particle sizes.

Future Research

The chromium concentrations found in the particles on the last six stages of the cascade impactor provide a set of data that may be useful in determining the respirable chromium exposure to a painter. The particle size distributions collected in this effort should not be interpreted as being representative of a painter's exposure since samples collected on a test stand may not accurately simulate the complex air flows around a painter. It would be valuable to compare the particle size distributions of this effort to actual breathing zone distributions in an attempt to refine the estimated exposure in terms of breathing zone distributions instead of area sampling distributions. This strategy would also provide an estimate to the question of how much chromium could actually be delivered to the pulmonary region during an exposure period.

Comparison of the results of this effort with area sampling results from operational paint booth activity at Air Force Bases would provide a valuable validation step to this data. The total chromium mass collected in the samples should correlate to area samples for total chromium mass in Air Force paint booths.

Other primer paints are used in Air Force painting operations and may differ from Deft 02-Y-040 primer in the amount of chromate present, overspray behavior, and even types of chromate used as the corrosion inhibitor. Other primers could be evaluated in the same manner to develop a database of chromium concentrations for all primers in the Air Force inventory.

This study was limited to a top cutpoint of 16.7 um. This cutpoint falls well below the upper size range for inhalable particles and does not characterize the full range of chromium concentrations that can deposit in the respiratory system. Considering that 80% of the collected mass was larger than 16.7 um, it would be beneficial to expand the cutpoint range of collected particles to cover the full respiratory system. This would provide a more comprehensive view of the deposition concentrations throughout the full respiratory system.

Appendix A

This table is the raw data from the data collection process.

- "Date" is the date each sampling event occurred.

- "ID" is the sample identifier for each sampling event.

- "Pre-weight" and "Dry-weight" show the gravimetric results for the cellulose substrates before and after sampling and dessication.

- "Mass Collected" is "Pre-Weight" subtracted from "Dry-Weight".

- "Dilution Ratio" shows the amount each sample was manually diluted in order to fall into the range of the analysis procedure. A value of 1 indicates that no dilution occurred.

- "Unadjusted Cr" shows the results taken directly from the atomic absorption software without compensating for manual dilutions

- "Adjusted Cr" is the "Unadjusted Cr" multiplied by "Dilution Ratio".

- "Mass Cr" shows the actual mass of chromium in each sample adjusted for the initial dilution by 5 ml of HNO_3 and 20 ml de-ionized water.

- "Cr Conc" is "Mass Cr" divided by "Mass Collected".

Date	ID	Pre - Weight	Dry - Weight	Mass Collected (um)	Dilution Ratio 1:X-1	Unadjusted Cr (ppm)	Adjusted Cr (ppm)	Mass Cr (ug)	Cr Conc (ug/mg)
14 Oct 99 PM	1-1	0.06155	0.07488	13330	4	9.682	**38.728**	968.200	72.633
14 Oct 99 PM	1-2	0.06491	0.06580	890	5	0.450776	**2.254**	56.347	63.311
14 Oct 99 PM	1-3	0.05747	0.05800	530	2	0.587818	**1.176**	29.391	55.455
14 Oct 99 PM	1-4	0.06187	0.06225	380	2	0.232274	**0.465**	11.614	30.562
14 Oct 99 PM	1-5	0.06478	0.06489	110	1	0.04972	**0.050**	1.243	11.300
14 Oct 99 PM	1-6	0.05748	0.05760	120	1	0.136234	**0.136**	3.406	28.382
14 Oct 99 PM	1-7	0.06140	0.06181	410	1	0.04723	**0.047**	1.181	2.880
14 Oct 99 PM	1-8	0.06918	0.06963	450	1	0.04353	**0.044**	1.088	2.418
14 Oct 99 PM	2-1	0.06481	0.06920	4390	1	13.596	**13.596**	339.900	77.426
14 Oct 99 PM	2-2	0.05721	0.05820	990	7	0.558773	**3.911**	97.785	98.773
14 Oct 99 PM	2-3	0.05880	0.05940	600	5	0.229190	**1.146**	28.649	47.748
21 Oct 99 AM	1-2	0.06269	0.06366	970	1	3.114	**3.114**	77.850	80.258
21 Oct 99 AM	1-3	0.06240	0.06301	610	1	1.186	**1.186**	29.650	48.607
21 Oct 99 AM	1-4	0.05755	0.05789	340	5	0.137190	**0.686**	17.149	50.438

21 Oct 99 AM	1-5	0.05755	0.05765	100	2	0.029576	**0.059**	1.479	14.788
21 Oct 99 AM	1-6	0.06165	0.06178	130	2	0.067181	**0.134**	3.359	25.839
21 Oct 99 AM	1-7	0.06013	0.06018	50	1	0.056421	**0.056**	1.411	28.211
21 Oct 99 AM	2-1	0.05743	0.06865	11220	3	9.944	**29.832**	745.800	66.471
21 Oct 99 AM	2-2	0.06272	0.06429	1570	1	4.352	**4.352**	108.800	69.299
21 Oct 99 AM	2-3	0.06242	0.06314	720	1	1.266	**1.266**	31.650	43.958
21 Oct 99 PM	1-1	0.05766	0.08519	27530	9	9.701	**87.309**	2182.725	79.285
21 Oct 99 PM	1-2	0.05843	0.05928	850	1	0.488	**0.488**	12.200	14.353
21 Oct 99 PM	1-3	0.06134	0.06198	640	7	0.249	**1.740**	43.506	67.977
21 Oct 99 PM	1-4	0.06403	0.06431	280	4	0.234	**0.935**	23.375	83.481
21 Oct 99 PM	1-5	0.06099	0.06112	130	1	0.257	**0.257**	6.423	49.409
21 Oct 99 PM	1-6	0.06229	0.06245	160	1	0.130	**0.130**	3.255	20.344
21 Oct 99 PM	1-8	0.07240	0.07250	100	1	0.104	**0.104**	2.600	25.998
21 Oct 99 PM	2-1	0.06338	0.07304	9660	3	8.905	**26.715**	667.875	69.138
21 Oct 99 PM	2-2	0.06228	0.06378	1500	1	4.280	**4.280**	107.000	71.333
21 Oct 99 PM	2-3	0.06246	0.06303	570	7	0.259	**1.811**	45.267	79.415
22 Oct 99 AM	1-1	0.05689	0.07654	19650	5	11.697	**58.485**	1462.125	74.408
22 Oct 99 AM	1-2	0.05756	0.05845	890	1	3.059	**3.059**	76.475	85.927
22 Oct 99 AM	1-3	0.05760	0.05805	450	5	0.271	**1.354**	33.843	75.206
22 Oct 99 AM	1-4	0.06196	0.06199	30	1	0.398	**0.398**	9.939	331.312
22 Oct 99 AM	1-5	0.06170	0.06180	100	1	0.129	**0.129**	3.234	32.340
22 Oct 99 AM	1-6	0.06308	0.06316	80	1	0.052	**0.052**	1.302	16.275
22 Oct 99 AM	1-7	0.06016	0.06019	30	1	0.038	**0.038**	0.950	31.679
22 Oct 99 AM	1-8	0.07283	0.07288	50	1	0.041	**0.041**	1.037	20.740
22 Oct 99 AM	2-1	0.05697	0.06329	6320	1	16.449	**16.449**	411.225	65.067
22 Oct 99 AM	2-2	0.06453	0.06571	1180	1	3.486	**3.486**	87.150	73.856
22 Oct 99 AM	2-3	0.06292	0.06319	270	5	0.424	**2.119**	52.964	196.164
22 Oct 99 PM	1-1	0.06399	0.08822	24230	7	9.649	**67.543**	1688.575	69.689
22 Oct 99 PM	1-2	0.06402	0.06479	770	8	0.277	**2.212**	55.301	71.819
22 Oct 99 PM	1-3	0.06339	0.06387	480	5	0.204	**1.022**	25.561	53.253
22 Oct 99 PM	1-4	0.05750	0.05779	290	4	0.108	**0.433**	10.823	37.322
22 Oct 99 PM	1-5	0.05741	0.05759	180	1	0.119	**0.119**	2.982	16.566
22 Oct 99 PM	1-6	0.06107	0.06121	140	1	0.046	**0.046**	1.159	8.280
22 Oct 99 PM	1-7	0.06217	0.06227	100	1	0.029	**0.029**	0.721	7.209
22 Oct 99 PM	1-8	0.07310	0.07327	170	1	0.046	**0.046**	1.140	6.705
22 Oct 99 PM	2-1	0.06137	0.07064	9270	3	8.106	**24.318**	607.950	65.583
22 Oct 99 PM	2-2	0.06315	0.06429	1140	1	3.328	**3.328**	83.200	72.982
22 Oct 99 PM	2-3	0.06093	0.06142	490	5	0.246	**1.230**	30.750	62.755
29 Oct 99 AM	1-1	0.06143	0.09007	28640	9	8.548	**76.932**	1923.300	67.154
29 Oct 99 AM	1-2	0.06164	0.06299	1350	1	2.678	**2.678**	66.950	49.593
29 Oct 99 AM	1-3	0.06126	0.06204	780	1	1.454	**1.454**	36.350	46.603
29 Oct 99 AM	1-4	0.06140	0.06186	460	7	0.074	**0.519**	12.971	28.197
29 Oct 99 AM	1-5	0.06132	0.06166	340	7	0.035	**0.245**	6.137	18.050
29 Oct 99 AM	1-6	0.06112	0.06126	140	1	0.172	**0.172**	4.295	30.677
29 Oct 99 AM	1-8	0.07339	0.07378	387	7	0.014	**0.095**	2.380	6.149
29 Oct 99 AM	2-1	0.06138	0.06939	8010	2	10.973	**21.946**	548.650	68.496
29 Oct 99 AM	2-2	0.06118	0.06280	1620	1	3.931	**3.931**	98.275	60.664

29 Oct 99 AM	2-3	0.06130	0.06210	800	1	1.553	**1.553**	38.825	48.531
2 Nov 99 AM	1-1	0.06101	0.06767	6660	2	9.754	**19.508**	487.700	73.228
2 Nov 99 AM	1-2	0.06100	0.06116	160	1	0.628	**0.628**	15.706	98.163
2 Nov 99 AM	1-3	0.06093	0.06099	60	1	0.345	**0.345**	8.622	143.705
2 Nov 99 AM	1-5	0.06104	0.06116	120	2	0.032	**0.063**	1.582	13.182
2 Nov 99 AM	1-8	0.06946	0.06956	100	1	0.126	**0.126**	3.146	31.461
2 Nov 99 AM	2-1	0.06088	0.06340	2520	1	7.082	**7.082**	177.050	70.258
2 Nov 99 AM	2-2	0.06081	0.06125	440	7	0.225	**1.576**	39.402	89.551
2 Nov 99 AM	2-3	0.06133	0.06153	200	3	0.188	**0.565**	14.134	70.669
Cartridge Filter Results									
14 Oct 99 PM	2-9	0.06920	0.07306	3860	1	8.923	**8.923**	223.075	57.791
15 Oct 99 AM	2-9	0.07325	0.08435	11100	3	10.45	**31.335**	783.375	70.574
21 Oct 99 AM	2-9	0.07266	0.09549	22830	7	9.261	**64.827**	1620.675	70.989
21 Oct 99 PM	2-9	0.07246	0.09175	19290	5	10.70	**53.490**	1337.250	69.323
22 Oct 99 AM	2-9	0.07305	0.08424	11190	3	11.434	**34.302**	857.550	76.635
22 Oct 99 PM	2-9	0.07431	0.08250	8190	2	11.745	**23.490**	587.250	71.703
29 Oct 99 AM	2-9	0.07320	0.09881	25610	8	9.221	**73.768**	1844.200	72.011
2 Nov 99 AM	2-9	0.07010	0.07998	9880	3	9.210	**27.630**	690.750	69.914

Appendix B

Equipment: The following is a list of the equipment that was used to complete the data collection and sample analysis for this thesis.

Table 11. Equipment

Equipment	Manufacturer	Model #	Serial #
SAMPLING EQUIPMENT			
Vacuum Pump	GAST	23 Series	00724996
Rotometer – 604	Matheson Gas Products	FM-1050B-HA	
Instruments Magnahelic (0-10 psi)	Dwyer	2210C	
Instruments Magnahelic (0-5 psi)	Dwyer	2205C	
plastic 3/8" tubing	Imperial Eastman	66-P-3/8	
plastic 1/4" tubing	Imperial Eastman	44-P-1/4	
7 stage cascade impactor	In-Tox Products	S	
7 stage cascade impactor	In-Tox Products	P	
Selectomite 2 way valve	Hoke	316SST	
Electric Timer	Gralab	625	701791
General Purpose Valve 104R	Automatic Switch.	8320B176	
Gilibrator, 2-30 lpm	Gilian Instruments	D800285	3655-H
Aluminum Filter Cartridge	Gelman Instruments	2220-1	
25 mm Mixed Cellulose Ester filters (0.1 μm)	Millipore		
47 mm Mixed Cellulose Ester filters (0.8 μm)	Millipore		
ANALYTICAL EQUIPMENT			
Microwave Digestion System	OI Analytical	7295	
Nitric Acid		Lab Grade	
Atomic Absorption Spectrometer	GBC	Avanta	
Forceps			
Scale			
PAINT		MSDS Date	
Mil-P-23377 Primer (2 part)	Deft 02Y040	2/27/97	

Appendix C

Graphite Furnace Parameters

These parameters are representative of a typical graphite furnace run. Approximately 20 runs were made during this effort that followed these parameters. A different calibration curve was generated for each run. A calibration curve representative of most analysis runs is shown in Figure 28.

Furnace Parameters				
Step	Final Temp. (C)	Ramp Time (s)	Hold Time (s)	Gas Type
Step 1 Inject Sample				
Step 2	80°	5	10	Inert
Step 3	130°	30	10	Inert
Step 4	1400°	15	15	Inert
Step 5	2500°	1.4	1.6	None
Step 6	2700°	0.5	1.5	Inert

Sample Measurement Parameters	
Measurement Mode	Peak Area
Sample Introduction	Automatic
Time Constant	0.0 s
Replicates	3
Dilution Factor	0.25
Maximum Dilutions	5

Instrument Parameters	
EHT approximately:	433 Volts
Each sample initially diluted by	1/2.
System Type	Furnace
Element	Cr
Matrix	Paint Sample
Lamp Current	6.0 mA
Wavelength	357.9 nm

Calibration		
Calibration Mode	Conc. Least Squares: Max Error: 3.958 R^2: 0.986	
Label	Conc. (ug/l)	Mean Abs.
Standard 1	10	0.14
Standard 2	25	0.269
Standard 3	40	0.563
Standard 4	55	0.701
Standard 5	70	0.973

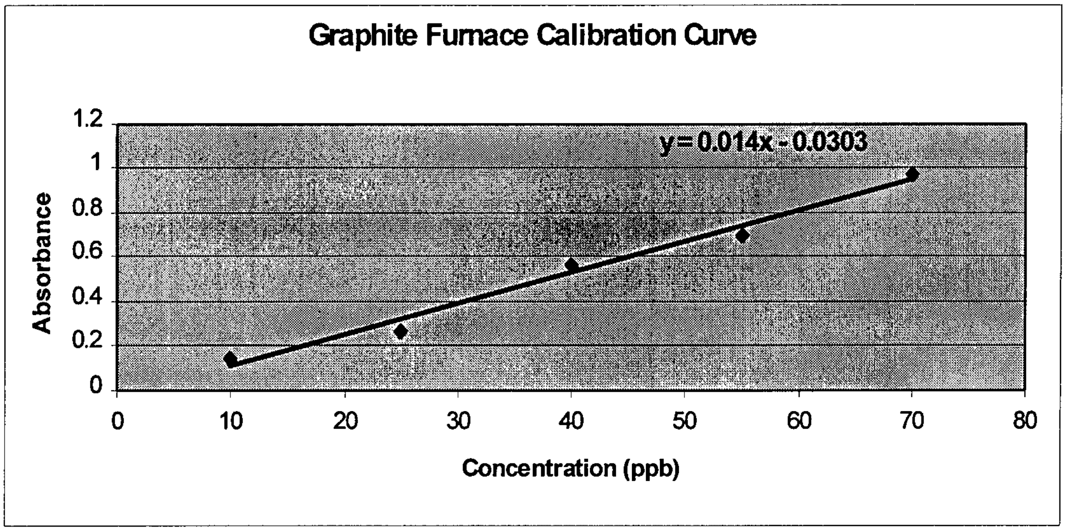


Figure 28. Representative Graphite Furnace Calibration Curve

There are several methods that can be used to calculate the detection limits for the calibration curve. The method used for this effort was to multiply the standard deviation of the sample blank by three times. Under this method, the lower detection limit was calculated to be 0.015 absorbance, which is converted to 0.0301 ppb.

The linear range of the calibration curve extended from 10 – 70 ppb. Beyond 70 ppb, it could not be assumed that the curve was linear, and readings that exceeded 70 ppb were not accepted. No matrix modifiers were added for the analysis procedure.

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ABSTRACT (*Maximum 200 Words)*

The purpose of this research was to determine if there a bias in the chromium concentration among particle sizes of aircraft primer overspray. It is often assumed that all particles in paint overspray have the same chemical composition as the original paint mixture, but differences in composition based on particle size may affect actual exposures. The research question was answered by executing a methodology that involved collecting particle size distributions, digesting the samples, and analyzing for chromium concentrations. The results showed a statistically significant difference between particle size groups above and below 2.5 um. Four times less chromium per unit solid mass collected is found in particles less than 2.5 um. Particles less that 2.5 um are more likely to deposit in the deeper pulmonary region of the lungs. The results of this experiment show that theoretical exposure calculations, which assume the same composition in a paint particle as the original paint mixture, may overstate actual exposures. The results of this study provide evidence that the concentration and mass of chromium deposited in the pulmonary region of the lungs may be significantly less than is deposited in the upper regions. This leads to the conclusion that pulmonary dosing may be less of an exposure hazard than would be concluded by assuming an equal distribution of chromium across all particle sizes.

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