CHROMATE DISSOCIATION FROM PRIMER PAINT IN SIMULATED LUNG FLUID

THESIS

Tiffany J. R. Morgan, Captain, USAF
AFIT/GEE/ENV/00M-14

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ABSTRACT (*Maximum 200 Words*)

OSHA has proposed a new strontium chromate exposure standard that would potentially cause Air Force paint facilities to be in violation of the proposed standard if adopted. This proposed reduction make the continued use of chromate containing primer paints very difficult. There is currently no acceptable replacements for chromate containing primer paints on AF aircraft. This study suggests that paint particles with chromate bound in primer paint may be unavailable for bodily absorption if inhaled and a reduced standard for painting applications may be unnecessary.

Primer paint overspray was collected into simulated lung fluid (SLF) and allowed 6 hr, 24 hr and 48 hr contact time in the SLF. At each residence time, particles wre filtered out and the dissolved chromate concentrations were quantified. The fraction of chromate dissolved was them compared to the total chromate originally collected. The results of this experiment imply that residence time in SLF does not affect dissociation. Results of the dissociation of chromate in primer paint particles implies the chromate dissociation may be hindered.

14. SUBJECT TERMS

Chromate, hexavalent chromium, strontium chromate, occupational exposure limit, simulated lung fluid, dissociation, primer paint overspray, corrosion control, Deft 02Y40, Courtalds 390x519, MIL-P-23377G, microwave digestion, atomic absorption spectroscopy

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Abstract

United States Air Force aircraft require a protective coating to prevent corrosion. Strontium chromate is an essential component in the primer paint to provide corrosion control. Occupational exposure limits to chromate are based on animal and epidemiological studies, which demonstrate that chromate is carcinogenic. Such studies may not accurately reflect the exposure of the USAF application method: spray painting. If chromate cannot dissociate from a primer paint particle, the particle may be cleared from the upper regions of the lung before chromate release can occur.

Paint overspray from two military specification primer paints was collected into a midget impinger containing simulated lung fluid (SLF). Particles were allowed to reside in solution for 6, 24, and 48 hours. At the end of each residence time, portions of the sample were filtered using a 2 μm Teflon filter. Chromate ions remaining in solution would pass through the filter while paint particles were left behind. Samples that were filtered represent chromate dissociated from the paint particles. Samples that were not filtered represent the total chromate concentration in the collected paint particles. Samples were decomposed by microwave digestion and analyzed for chromium by atomic absorption spectroscopy. Comparisons were made among the three filtered samples and corresponding unfiltered sample.

50% of the first manufacturer (Deft) samples were lower in chromium concentrations in filtered samples when compared to the respective unfiltered samples. 67% of the second manufacturer (Courtalds) samples showed the same reduced chromium concentrations in filtered samples compared to respective unfiltered samples.

The reduced chromium concentrations in filtered samples imply that chromium bound in the two tested primer paints may influence chromium dissociation. Studies of chromium dissociation and related fields may prove fruitful in developing a new chromium occupational exposure limit tailored to exposure from painting operations.

CHROMATE DISSOCIATION FROM PRIMER PAINT IN SIMULATED LUNG FLUID

I. Introduction

Air Force Primer Paint Overview

The aluminum skin of United States Air Force (USAF) aircraft would be vulnerable to corrosive oxidation if not properly maintained by routine inspection and painting cycles. Military aircraft are especially vulnerable to weakening from corrosion because the skin of military aircraft is relatively thin to reduce weight. Therefore, the routine painting is critical to the life and performance of military aircraft. The primer paint provides a better adherence surface for the polyurethane topcoat. The primer paint also provides the most protection from aluminum oxidation and corrosion (TO 1-1-8, 1998:1-1). The component responsible for this corrosion control is typically barium chromate or strontium chromate.

There are two military specifications and one federal specification that regulate primer paint: MIL-P-23377G, MIL-P-85582B, and TT-P-2760A respectively. Each of these three specifications contains two classes of primer paint: strontium chromate based and non-chromate based. The two military specifications state that chromated paint is to be used unless a non-chromated paint is specifically authorized by procuring activity or

engineering authority for system or item. Despite inclusion of non-chromated paints in the primer coating specifications, their use is practically non-existent.

Chromium Health Hazards

Although strontium chromate provides qualities desirable for protecting the aircraft skin, there are health and environmental concerns with this chemical. Based on human data, hexavalent chromium was found to be a carcinogen (IARC, 1990:213). Therefore, working with hexavalent chromium poses a substantial health risk if not done properly.

Chromium is found naturally in the earth's crust; trivalent chromium is a necessary dietary mineral. Other oxidative states such as hexavalent chromium can be hazardous to human health. Occupational exposure limits for chromium have been set by the Occupational Safety and Health Administration (OSHA), American Conference of Governmental Industrial Hygienists (ACGIH) and National Institute of Occupational Safety and Health (NIOSH). While some epidemiological studies have been conducted with respect to occupational chromium exposure, no health studies have been conducted for the USAF method of application: spray painting (IARC, 1990:85-98).

Chromated Paint Alternatives

Prompted by the fact that hexavalent chromium is a carcinogen, the USAF is seeking alternatives to chromated primer paint. Boeing Company Aircraft & Missiles has researched possible substitutes for chromate containing primers for corrosion control. One Boeing report identified likely candidates to replace chromated primers. A subsequent report evaluated those candidates and narrowed the choices to be applied to operational aircraft for further evaluation. Successful results would provide the USAF

with viable alternatives to chromated primer paint (NDCEE1 & 2 1998: 1,1). However, it is anticipated that chromated primers will be used on USAF aircraft well into the future.

Occupational Exposure Concerns

The current occupational exposure limit for chromium has been challenged. A reduction of the hexavalent chromium permissible exposure limit (PEL) from 100 $\mu g/m^3$ (ceiling) to 0.5 $\mu g/m^3$ eight-hour time-weighted average (TWA) has been requested. The Occupational Safety and Health Administration (OSHA) has denied the emergency request but a rulemaking procedure has been instigated and a proposed rule is being investigated (Federal Register 64: 21485, 1999:Section 6(b)). To accurately assess the need for a revised chromium exposure limit, it is necessary to review the human health concerns of chromium. One avenue of information is relevant animal studies.

Relevant Animal Studies

A major study that influenced the American Conference of Governmental Industrial Hygienists (ACGIH) exposure limit was conducted in 1986 by Levy and colleagues. In the Levy study, one chromate doped pellet was surgically implanted in one lung of each experimental rat. Of the 21 chromium containing treatments tested, only two types of compounds resulted in significantly elevated lung tumors: strontium chromate and zinc chromate (Levy, 1986:243). Although the Levy study provides evidence that strontium chromate is a carcinogen, the exposure method used in this study does not accurately reflect the type of chromate exposure seen with primer paints.

Another study evaluated the gastrointestinal uptake of chromium by feeding rats with unencapsulated and silica encapsulated chromium (Clapp, 1991:271). Rats were fed

chromium concentrations for one month during which blood samples were collected periodically. The animals were allowed a two-week recovery time and then sacrificed. Analyses were performed on the rats' blood samples and kidneys (post-mortem) to evaluate for contaminant concentration. The rats fed with encapsulated chromium had significantly less chromium in the kidney than rats fed non-encapsulated chromium (Clapp, 1991:272-273, 275). This indicates that encapsulation of chromium may hinder chromium absorption by living tissue.

Unfortunately, there may be a bias introduced by applying this type of study to exposures that may occur during painting applications. Oral and lung implantation techniques do not adequately reflect the release of chromate from a paint particle in the lung. Also, the quantity of encapsulated chromate may vary greatly across primer paint matrices and is not adequately represented by silica. These studies do not include natural lung expulsion of foreign particles nor do they address particle size in relation to deposition in the lung.

Thesis Objective

The objective of this study is to determine dissociation of chromate in simulated lung fluid (SLF) if the compound is bound in paint particles. Primer paint overspray was collected into SLF, targeting inhalable sized particles. After each residence time of the particles in the SLF (6, 24 and 48 hours), a portion of the sample was filtered. The amount of chromate in the unfiltered and the filtered sample was quantified using platform stabilized graphite furnace atomic absorption spectrometry. Statistical testing was applied to compare the filtered samples to the respective unfiltered sample. If the statistical results indicate that dissociation of chromium is hindered when bound in paint,

chromate containing primer paints may not be as great a hazard as initially predicted in the studies summarized in the literature review. If chromated primer paint does not dissociate as readily as pure chromate compounds, a stricter chromium standard may be unnecessary when chromate exposure is from painting applications.

Research Goals

This research study focuses on three primary research goals. The first objective was to develop a method for testing dissociation in simulated body fluids. Direct collection into a simulated fluid required an impinger. To target respirable particles, a cyclone was incorporated in series prior to the impinger. This set-up should result in the collection of respirable particle sizes in simulated body fluid.

A second query was whether residence time significantly affects the dissolution of chromate. Contact time with simulated body fluid may have a distinct affect on chromate dissolution. To determine whether time had such an influence on dissolution, several residence times were observed and analyzed. Collected samples were split such that portions of each sample were allowed 6, 24 and 48 hour residence times with the simulated fluid. Samples were analyzed for differences between residence times.

The final objective of this thesis was to evaluate the relative amount of chromate that dissociates from the collected primer paint sample. Each sample was filtered at the three different residence times to isolate chromium ions. The three filtered samples were compared to the unfiltered sample. The comparison of filtered to non-filtered sample indicates the amount of chromate dissociation from primer paint bound in SLF.

II. Literature Review

Overview

This literature review will first explore the USAF background concerning the use of primer paints. A cursory background of chromium is discussed. Next is a discussion of the regulatory limits for chromate exposures as well as current legislation pertaining to those exposure limits. Chromated primer paint alternatives are addressed. Pertinent lung physiology and animal studies will be explored. Information concerning industry standards for quantifying occupational exposure and personal protective equipment capabilities and limitations will be discussed. Finally, the methodology of this thesis is outlined.

Background

United States Air Force (USAF) aircraft surfaces are subjected to hostile environments. Protecting aircraft surfaces is vital to maintaining their integrity. Inadequate control and prevention of corrosion can hinder the USAF mission and potentially compromise safety. The primary protection for the aircraft skin is the paint. The performance of the paint coating is critical to extend the life and performance of military aircraft. The primer paint serves two purposes. The first purpose is to provide a better surface to which the polyurethane topcoat adheres. The second purpose is to protect the metal skin from excessive corrosion by preventing aluminum oxidation (TO 1-1-8, 1998:1-1). The component responsible for this corrosion control is typically barium chromate or strontium chromate.

USAF Primer Paint

There are two military specifications and one federal specification that regulate primer paint: MIL-P-23377G, MIL-P-85582B, and TT-P-2760A respectively. The most heavily used primer for aircraft application is MIL-P-23377G (Weissling, 1996:61). It is a solvent based epoxy primer paint with adhesion properties and is very resistant to chemicals, lubricants and corrosive atmospheres. Primer MIL-P-85582B is a water-based epoxy primer formulated to meet most local environmental pollution regulations (low volatile organic compounds [VOC]). TT-P-2760 primer paint is a polyurethane paint designed for high flexibility on unique surfaces (TO-1-1-8, 1998:4-7).

Each of the three specifications classifies paint with two designators (type and class) resulting in four possible combinations. The two types are standard pigments (I) and low infrared reflective pigments (II). The two classes are chromate-based (C) and non-chromate based (N) corrosion inhibitors. Chromate based paints are further broken down into barium chromate ($BaCrO_4$) or strontium chromate ($SrCrO_4$). Strontium chromate is the preferred corrosion inhibitor (CTIO, 1999).

Although a non-chromated paint class exists in each specification, only MIL-P-85582B includes a single non-chromated paint on its list of approved paints. The two military specifications state that chromated paint is to be used unless a non-chromated paint is specifically authorized by procuring activity or engineering authority for the system or item (MIL-P-23377G, 1994:1; MIL-P-85582B, 1994:1). Despite non-chromated paint classifications in the primer coating specifications, their use is practically non-existent. Table 1 shows the aircraft exterior coating specifications.

Table 1. Aircraft Exterior Coating Specifications

Military Specification	Constituent			Paint Type
	$BaCrO_4$	$SrCrO_4$	Non-Chromate	
MIL-P-23377G	N/A	Class C	Class N	High Solids Epoxy
MIL-P-85582B	Class 1A	Class 1B	Class 2	Waterborne epoxy
TT-P-2760A	N/A	Class C	Class N	High Solids Polyurethane

C = Chromated Paint N = Non-chromated Paint

To maximize aircraft painting operations, the Coating Technologies Integration Office (CTIO) at Wright-Patterson Air Force Base (WPAFB), OH was created to test paint systems. The CTIO tests and evaluates materials and processes for aircraft painting and de-painting operations. The CTIO is responsible for identifying materials that meet military specifications and integrating advancements into routine USAF practice. An initial tasking of the CTIO program was to baseline the paint and associated products usage rates in 1995. The aggregate paint usage study concluded all primer paints contained chromate (mainly strontium chromate) (CTIO, 1999).

Chromate

Chromate is a critical component of primer paint. When the paint on the aircraft suffers weathering such as surface cracks the chromate compound leaches into the crack to prevent corrosion and protect the aircraft surface. No substance has been found to provide corrosion protection like chromate (CTIO, 1999). Due to its critical role in primer paint, a brief background of chromium is provided.

Chromium (Cr) is found naturally in the earth's crust in minerals like chromite and chrocoite (Marqués, 1998: 239). It is the sixth most abundant resource and most commonly found in three oxidative states: 0 (elemental), III, and VI. Very small amounts

of Cr (III) are a necessary dietary mineral for glucose metabolism. Cr (VI) is a common oxidative state of the chromate associated with occupational chromium exposures. Occupational exposures to chromium can include welding, leather tanning, electroplating, textile manufacturing, photoengraving, copier servicing and paints/pigments (ATSDR 1990:2,3; IARC, 1990:24). Detailed chromium studies have been conducted in the following areas: ferrochromium steel and high chromium alloy production, production of chromates and chromate pigments, leather tanning, chromium plating and welding. Unfortunately, no detailed health studies have been conducted for spray paint operations (IARC, 1990: 85-98). The health effects of chromium are of great concern to occupational workers potentially exposed to chromium. The toxicity of the chromium component depends on both oxidation state and solubility (Ballantyne: 1995:25).

The oxidative state of chromium in barium chromate and strontium chromate is hexavalent chromium: Cr(VI). There are many health hazards associated with Cr(VI). Cr (VI) compounds are oxidizing agents that can induce tissue damage directly. *In vitro* studies have shown that Cr(VI) directly induces nephrotoxicity and hepatoxicity. Cr(VI) increases cancer risk by the increased formations of DNA adducts, radical adducts, DNA cross-links and DNA strand breakage interference with normal DNA template replication and transcription (Dartsch, 1998: S40-41). Cr(VI) is classified as carcinogenic to humans (IARC, 1990:214).

Strontium chromate is created by adding a solution of strontium salt to a solution of sodium chromate. Its molecular formula is $SrCrO_4$. It is a yellow crystalline powder considered insoluble in water but soluble in hydrochloric, nitric and acetic acids and ammonium salts. Common synonyms are chromic acid and strontium salt (IARC,

1990:58,77). Strontium chromate was originally used as color in artist's paints but later became primarily used for its corrosion resistance on aluminum and magnesium alloys. It is also a chemically resistant coating due to low reactivity. Electroplating industries use strontium chromate to control sulfate content in electroplating solutions (IARC, 1990:84). International Agency for Research on Cancer (IARC) epidemiological studies are broken into five major categories: ferrochromium steel and high chromium alloy production, production of chromates and chromate pigments, leather tanning, chromium plating, and welding. Spray painting is not evaluated as a separate category or in detail but listed as extra miscellaneous data under "other occupations" (IARC, 1990:85-98). Lack of spray painting epidemiological studies means regulatory exposure limits may not have the most relevant information upon which to base exposure limits.

Regulatory Exposure Limits

Chromium exposure limits have been a recent topic of discussion in industry as well as in regulating agencies. In July 1993, two occupational worker organizations joined forces to elevate the health hazard concerns of working with hexavalent chromium. The Oil, Chemical and Atomic Workers International Union (OCAW) and Public Citizen's Health Research Group (HRG) petitioned the Occupational Safety and Health Administration (OSHA) for an emergency temporary standard (ETS) for occupational exposures to hexavalent chromium. OCAW and HRG requested a reduction to the permissible exposure limit (PEL).

Three agencies issue occupational exposure regulation for hazardous materials: OSHA, NIOSH, and ACGIH.

OSHA Chromium Exposure Limit.

OSHA is the only agency that regulates occupational exposures for industry with legal enforcement. Compliance with OSHA is legally required. OSHA's goal is to protect the occupational worker from hazardous materials but must include feasibility when determining exposure control in industry. OSHA's permissible exposure limit (PEL) for chromate is unchanged since 1971 (Martonik, 1995). The current PEL is 100 $\mu g/m^3$ as a ceiling value as defined by Chapter 29 Code of Federal Regulations Part 1910 Subpart 1000 (29 CFR 1910.1000) Table Z for "Chromic acid and Chromates as (CrO_3)". Though OSHA denied the OCAW/HRG emergency request, a rulemaking procedure is in place and a proposed rule is in being investigated (Federal Register 64: 21485, 1999:Section 6(b)). In anticipation of a reduced hexavalent chromium PEL promulgation, OSHA also revised the detection method used to quantify chromium so that the method can resolve the lower detection limit needed for the lower PEL (OSHA Method 215, 1998:3).

ACGIH Chromium Exposure Limit.

The ACGIH is a private, professional organization. ACGIH is concerned with the exposure to which a worker may be exposed without adverse affect. ACGIH provides guidelines by which industry may voluntarily follow. "Ceiling" is defined by ACGIH as the concentration that should not be exceeded during any part of the workday. A time-weighted average (TWA) is an occupational exposure averaged over the conventional 8-hour workday and 40 hour work week (ACGIH 1998:4-5). ACGIH has chromium standards for three oxidative states as well as strontium chromate. The soluble and

insoluble forms are classified as confirmed human carcinogens. Strontium chromate as Cr (VI) is classified as a suspected human carcinogen due to limited human evidence and sufficient exposure evidence in animals (ACGIH, 1998:26,63,74). ACGIH based this decision primarily on the Levy study described in more detail later.

NIOSH Chromium Exposure Limit.

NIOSH is a governmental organization that is primarily concerned with preventing occupational disease. Recommendations for exposure limits are not legally binding to industry, nor do they take into account the feasibility of suggested exposure limits. NIOSH has a ceiling for chromates and two TWAs: one for Cr (VI) as well as one for (0) and (II). The TWAs are based on the lowest detection limit (NIOSH, 1997:70-71,351).

Current chromium exposure limits are identified by organization in Table 2.

Table 2. Comparison of Agency Exposure Limits for Chromium

Limits	As in Cr(VI) mg/m^3		As in CrO_3 mg/m^3 *	
	Ceiling	TLV-TWA	Ceiling	TLV-TWA
OSHA			0.1	
ACGIH		0.0005**		
		0.05 (8 hr)		0.5 (0) or (II)
				0.05 (soluble)
				0.01 (insoluble)
NIOSH	.05	.025 (10 hr)		
		.001 (10 hr)***		

*0.05 mg/m^3 as Cr (VI) equates to 0.01 as CrO_3
** Indicates a strontium chromate exposure limit
*** Indicates insoluble (carcinogenic) chromium forms based on lowest detection limit

Chromated Primer Paint Alternatives

The health concerns associated with chromium have led the USAF to search for alternatives. Boeing Company Aircraft and Missiles has researched possible substitutes

for chromate containing primer paints for corrosion control. One Boeing report identified likely candidates to replace chromate containing primer paints. A subsequent report evaluated those candidates and narrowed the choices to be applied to operational aircraft for further evaluation. Successful results would provide the USAF with viable alternatives to chromated primer paint (NDCEE 1 &2, 1998:1,1). However, it is anticipated that chromated primers will be used on aircraft well into the future (CTIO, 1999).

Inhalation Toxicology/Lung Physiology

There are three primary routes of exposure to toxic substances: inhalation, ingestion and dermal absorption. Spray painting is the primary application of concern therefore this thesis will address strictly the inhalation route.

Inhalation exposure to particulates primarily affects the respiratory system. The respiratory system is comprised of a conducting zone and a respiratory (gas exchange) zone as illustrated below in Figure 1 (Fox, 1996:460-1).

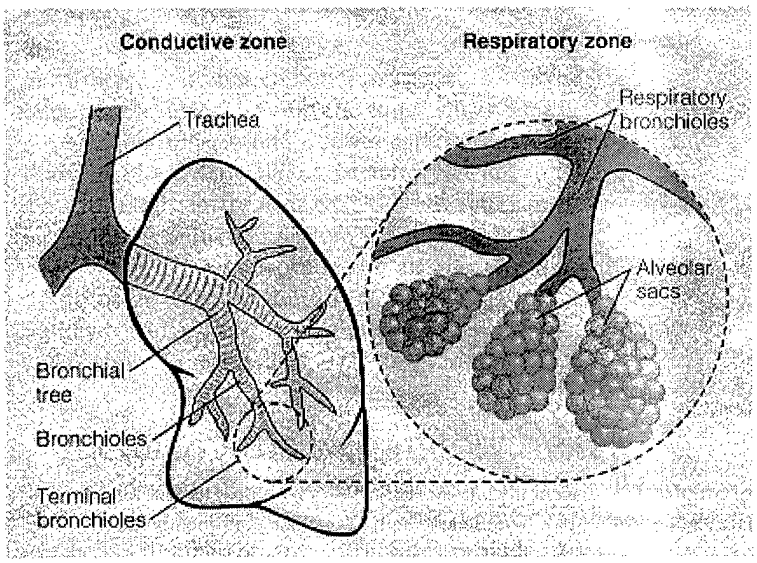


Figure 1. Conducting and Respiratory Zones (Modified from Fox, 1996: 462)

Conducting Zone

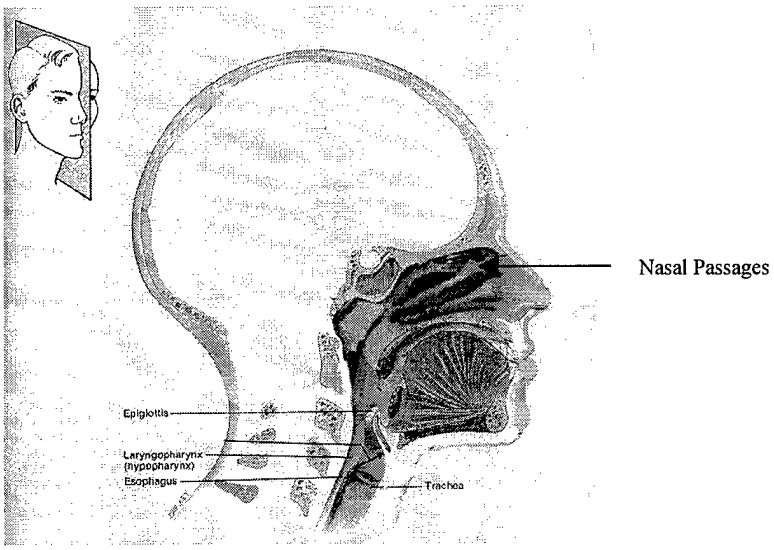


Figure 2. Cross-Section View of Upper Respiratory System (Modified from Tortora, 1992: 631)

Air first travels through the nasal passages (or mouth), pharynx and larynx. In this upper region, large airborne particles are filtered from the air and the air is warmed and partially humidified. Cilia are hair-like extensions on the surface of the airways. Cilia lining the posterior third of the nasal cavity move captured particles approximately 1.0 cm/min to a point to be swallowed. The pathways for air entering the nasopharynx turn sharply downward so larger particles are impacted on the surface. The epiglottis lies at the end of the nasopharynx region and provides a doorway to the larynx and trachea or esophagus. Particles impacted in the larynx are moved upward by mucus to be swallowed. The larynx also acts as an inspiratory air jet forcing larger particles to impact the trachea (Phalen, 1995:133-5).

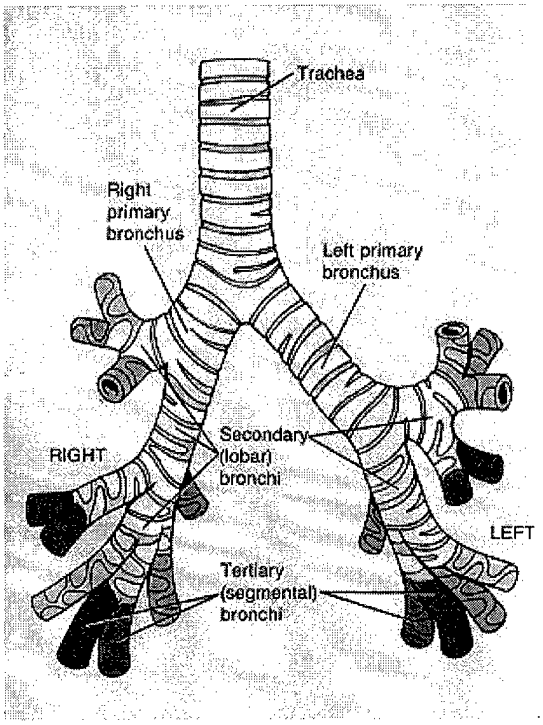


Figure 3. Successional Lung Branches (Modified from Tortora, 1992: 642)

Next the air passes through the trachea and bronchi. The primary bronchi (the first two lung branches) split into successional bronchi, further split to bronchioles and finally terminal bronchioles as illustrated in Figure 3. Each bifurcation leads to impaction of larger particles which are unable to negotiate the sharp turn in the lung passageway. The previously described sections comprise the conducting zone. The primary role of this zone is to warm, humidify, filter and clean the air prior to reaching the respiratory zone. Rarely do particles greater than $6_{\mu}m$ succeed in traveling to the respiratory zone (Fox, 1996:463).

Clearance of foreign particles in the lung can be accomplished by three major methods: mucociliary clearance, phagocytosis (mainly in alveoli) and coughing (Bouhuys, 1977:293). The clearance times commonly observed during mucociliary clearance are used as SLF residence times during this thesis effort.

Mucociliary Escalator Clearance

Mucociliary clearance occurs in the airways down to the to the primary bronchioles (conducting zone). The mucociliary system traps and sweeps away bacteria, inhaled particles and cellular debris (Bates, 1989:69). The upper layer in the epithelium are ciliated columnar cells interspersed with goblet cells, while the lower layer consists of intermediate and basal cells as shown in Figure 4 (Bates, 1989:69-70). This cell arrangement allows the production of mucus to reach the surface and the cilia to move foreign particles up and out of the conducting zone. Further down the lungs, the mucociliary clearance mechanism is unsuccessful because ciliary movement is ineffective and mucus production is lacking (Bouhuys, 1977:294).

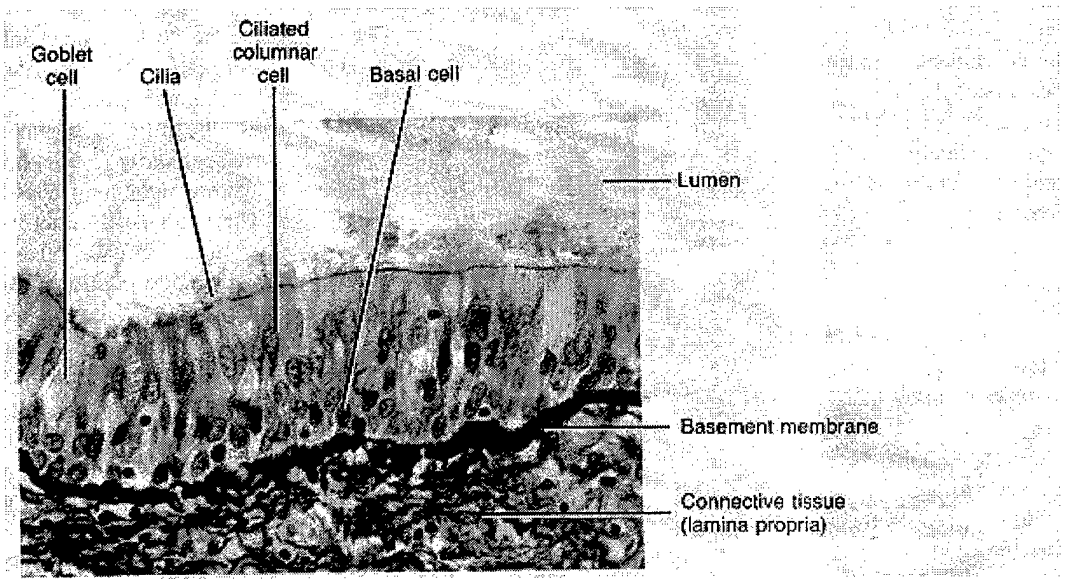


Figure 4. Mucociliary System Components (Tortora, 1992: 637)

Cilia are longer in the trachea (6 μm) and become increasingly shorter in the lower branches (3.6 μm) (Bates, 1980:70). Ciliated cells comprise 53% of cells lining the trachea, but the fraction decreases to 15% in the fifth bifurcation. There are two layers of

fluid that line this area of the respiratory system. The fluid at the base is serous and has viscosity similar to water (non-viscous). The fluid on top is mucus and is very thick (viscous). This thicker mucus created by the goblet cells and subepithelial glands captures many particles upon impact by design (Bates, 1989:70). The source of serous fluid is unknown. The cilia move forward in a slightly non-synchronized manner for the power stroke. The cilia are stiff, fully extended and make contact with the surface of the mucus layer. Recovery is a bending or doubling over which returns the cilia to the original starting point through non-viscous fluid. Linear velocity of the mucus layer is influenced by ciliary beat frequency. In this manner, the half-time clearance rates range from approximately 3 minutes in the trachea to 80-300 minutes in the lower bronchi (Bates, 1989:4).

The Respiratory Zone.

The respiratory zone includes the respiratory bronchioles, alveolar ducts, alveolar sacs and alveoli. This is where gas exchange from air to blood occurs. Main clearance mechanisms in this alveoli region are macrophagic and slower than ciliated sections of the lung. Macrophagic activity brings the particle or foreign matter into the cell and breaks it down. Ciliated sections clear particles quicker because the particle is simply moved from one place to another to be swallowed or expectorated. In contrast, decomposition of particles by macrophages is relatively time intensive. Clearance in between the macrophagic and ciliated regions is not clearly understood (Bates, 1989:4). Alveolar macrophages populate the alveoli. They engulf foreign particles by phagocytosis, pinocytosis and endocytosis. In endocytosis, the plasma membrane

surrounds the substance, encloses it and brings the substance into the cell. Phagocytosis occurs when projections of the cytoplasm engulf solids and bring the encased solid into the cell to be digested by enzymes encased in the vesicle with the solid(s). If the foreign body is a small liquid, the drop will be attracted and adhere to membrane surface. The membrane surface invaginates and brings the liquid into the cell. This process is called pinocytosis (Tortora, 1992:34). Through these processes, the alveolar macrophages keep the alveolar lining cleared of impurities that may try to enter the body (Phalen, 1995: 132). If a chromate containing paint particle were to reach this level of the lung, the macrophages would most likely engulf it and eventually break down the components.

This thesis effort focused on chromate dissociation of paint particles that may impact in the mucociliary escalator region. The experimental approach assumed residence time with SLF similar to clearance times in the mucociliary escalator.

Particle Size Deposition in the Lung

Particles greater than 50 μm generally do not enter the respiratory system. Particles larger than 10 μm are generally deposited in the upper respiratory tract while those between 2 and 10 μm reach the trachea and the bronchioles. If the MMAD is less than 1.2, the particle has a great possibility of deposition in the alveoli (Ballantyne, 1995:25). These values are illustrated in Figure 5.

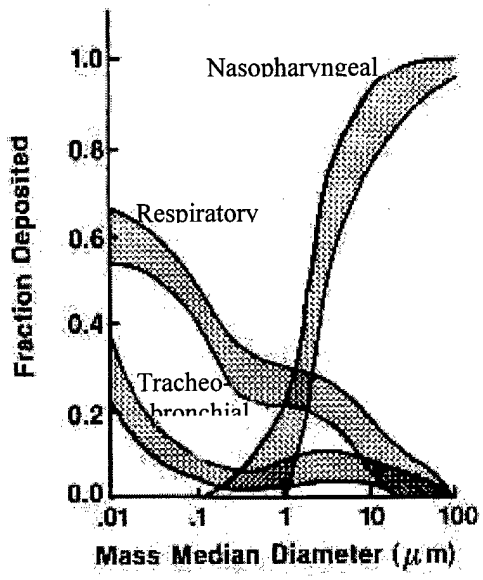


Figure 5. Fraction of Particle Deposition in Respiratory System

(Godish, 1991: 156)

Studies Contributing to Chromate Limits

To accurately assess the need for a revised chromium exposure limit, it is necessary to review the human health concerns of chromium. One avenue of information is relevant animal studies.

Animal Inhalation Study for Chromate Pellets.

The primary study upon which ACGIH based its recommendation for strontium chromate exposure limits is a 1986 study by Levy and colleagues. This animal study implanted an intrabronchial pellet in the left bronchus of each rat. The pellet was contained within a wire mesh suspended in a rat's lung. The pellets were impregnated with a mixture of cholesterol and one of 21 chromate compounds. This technique allowed the test material to leach to the lung tissues. Rats dosed with three specific

combinations (2 strontium chromate and 1 zinc chromate) developed statistically significant bronchial tumors (Levy, 1986:243).

While there is little controversy that strontium chromate is carcinogenic, this study may not reflect the type of exposures that painters may confront. The pellet implantation ignores the clearance mechanisms inherent in the respiratory system to expel contaminants. Additionally, in the Levy study the presentation of strontium chromate to lung tissue is a free form of strontium chromate. Occupational exposures to strontium chromate from primer paint overspray will be strontium chromate mixed with other paint components that may bind the chromate. The difference between free form and primer paint bound dissociation could influence whether the lung tissue will be exposed to strontium chromate from paint particles.

Particles inhaled may mucociliate up the respiratory pathways and then be swallowed. Once swallowed, the particles enter the intestinal tract. Therefore, an ingestion study would be relevant to explore the affects of chromium in the intestinal tract. One such study was conducted by Clapp and colleagues in 1991.

Animal Ingestion Study with Encapsulated Chromate.

Clapp and colleagues conducted an ingestion study for lead and chromium. This thesis is interested only in the chromium results so the lead results will not be presented. The Clapp study orally dosed laboratory rats 5 days a week for 4 weeks with encapsulated and non-encapsulated chromium in pigment materials. Following the 4 weeks of doses, a two week recovery period was allowed prior to animal sacrifice. Each rat was dosed with 1 milliliter (ml) of corn oil mixed with the pigment materials per 100

grams (g) of body weight. The standard to which the results were compared was a lead carbonate pigment. Lead chromate and a silica coated "chrome yellow" pigment were examined (Clapp, 1991:271). Concentrations varied such that each rat received 150 milligram (mg) Pb per kilogram (kg) of body weight. The chromium concentrations administrated to each animal were not standardized as the treatments were balanced for lead. The experimental schedule is outlined in Table 3.

Table 3. Clapp Ingestion Study Schedule of Experiment Actions

Week	Action
1	Chrome Concentrations Administered to Animal
2	Chrome Concentrations Administered to Animals
	Blood Samples Drawn
3	Chrome Concentrations Administered to Animals
4	Chrome Concentrations Administered to Animals
	Blood Samples Drawn
5	Recovery
6	Blood Samples Drawn
	Animals Sacrificed and Kidneys Removed

Blood, due to its importance in metals transport, and the kidney, due to its excretory function and elevated rate of metals accumulation, were sampled to evaluate chromium content. Chromium levels in the blood were not detected (10 microgram per liter (μg/l) detection limit). Only results from the female kidneys provided detectable chromium levels. An analysis of variance was performed on the chromium concentration results. In comparing the encapsulated and control results, there was no statistically significant difference in kidney chromium concentrations. However, there was a statistically significant difference in kidney chromium concentration when the unencapsulated and control results were compared. The study concluded that chromium

encapsulated by silica was less bioavailable than unencapsulated chromium (Clapp, 1991:274-275).

One corollary objective of this thesis is to determine whether the dissociation of strontium chromate in SLF differs from the dissociation of strontium chromate in water. The Clapp and colleagues study parallels this interest by seeking whether the body could absorb the chromium contaminant when bound in silica. Silica encapsulation simulates a paint matrix surrounding strontium chromate in primer paint. However, the chemical properties of silica do not accurately represent the paint matrix typically found in primer paint. Observing the dissociation of strontium chromate from primer paint overspray should provide information concerning paint matrix encapsulated particles. In addition to animal studies, epidemiological studies are very useful in determining some affects of occupational exposure to chromium on the human body.

Epidemiology Studies for Chrome Exposures.

Numerous epidemiological studies have been conducted for chrome production, manufacturing, pigment production, ferrochromium production, stainless steel, electroplating, chrome plating, leather tanning (IARC, 1990: 85-97). Few studies have approached the topic of spray painting. Of the small number of chromate studies that do speak to spray painting, most studies evaluate zinc chromate (Kano, 1993:16; Dalager, 1980:25; Kominsky, 1978:1). Two spray paint studies evaluated chromate but did not focus on lung affects nor did they distinguish the chromium source (Rosensteel, 1974:1; Chiazze, 1980:520). Epidemiological studies evaluating the effect of strontium chromate

occupational exposures on the human lung would be beneficial to determine the health effects.

Respiratory Protection

One challenge to industry with a revised chromium PEL will be adequate personal protection to meet that lower regulatory standard. Since the painting process cannot be easily altered to lower occupational exposures below the occupational limit, personal protective equipment (respiratory protection devices) is usually required. Federal guidance for respirators is found in 29 CFR 1910.134, Respiratory Protection. AF guidance, which is equal to or more stringent than Federal guidance, is found in Air Force Occupational, Fire, Safety and Health Standard (AFOSH STD) 48-1, Respiratory Protection Program. Each type of respirator has an assigned protection factor (APF). Greater APF values mean greater protection to the worker in general but the APF must be compared to the potential occupational exposure to determine if the respirator will properly protect the worker. To quantify potential occupational exposure, a Hazard Ratio (HR) must be calculated. The HR equation is listed below.

$$HR = \frac{\text{Measured Contaminant Concentration}}{\text{Contaminant Exposure Limit}}$$

The APF must be greater than the HR for the device to provide adequate protection to the occupational worker (AFOSH STD 48-1 1994:11).

Excluding self-contained breathing apparatus, the highest APF a respirator can provide is 1000 (AFOSH STD 49-1 1994:Atch 5). Currently, the AF can adequately protect painters from strontium chromate. Chromium concentrations from painting applications can reach and potentially exceed 1000 parts per million (ppm) (LaPuma,

1999: 687). With such high potential occupational exposures, if the PEL were lowered, adequate respiratory protection would be extremely difficult if not impossible.

Methodology

It was desired to mimic inhaled particles impacting the lung surface as well as incorporate industry standard collection procedures into the method. The devices decided upon were the impinger and the cyclone. Since several SLFs are used in the field, it was necessary to discriminate among them and select the best formulation. Not all primer paints could be sampled and analyzed; therefore, only two paints were chosen for the purpose of this thesis.

As discussed earlier, inhaled particles are allowed passage based on particle size (or mass median aerodynamic diameter (MMAD)). Particles may impact the surface of the lung if they do not successfully navigate the turns in the lung passages. The cyclone separates particles by size based on momentum. The air entering the inlet is drawn into a funnel due to the design of the cyclone. The larger particles are flung to the sides of the cyclone while the smaller, lighter particles float upward with the air current. In this manner, particles similar to inhaled particle sizes are selected. A cascade impactor would have provided more definitive particle size selection. However, cascade impactors are not normally used to collect routine occupational worker exposure samples and it would have been more challenging to arrange for the particles to collect in a fluid.

To simulate the impact of inhaled particles on lung fluid, the collected air needed to ultimately contact a liquid. In the lung, a particle will impact the lung fluid but only a small portion of the particle surface would contact the liquid. In this study, the particle would be immersed in the liquid. A midget impinger was selected to hold the SLF. This

small device is commonly used to entrain aerosols in liquid. The impinger draws air through tubing into a collection liquid. The collected air is scrubbed by the surrounding liquid and traps the contaminant in the liquid. Efficiencies of the impinger are not addressed as total chromium content is not a goal in the thesis experiment. It is assumed that the percent capture of chromium among collection impingers is constant and therefore the chromium concentrations can be compared.

The primer paints used for this thesis were selected based on which primer paints are most heavily used for painting USAF aircraft. Military specification MIL-P-23377G paint is most widely used during USAF aircraft painting operations. Deft and Courtalds are the most highly used MIL-P-23377G primer paints so they were chosen for collecting primer paint overspray (CTIO, 1999). The manufacturer formulation codes for Deft and Courtalds are 02Y40 and 519x390 respectively.

III. Methodology

Overview

The methodology section describes the equipment and methods developed to complete this research effort. The selections for residence times and sample digestion are discussed. The equipment used to discriminate particle size is described as well as the peripheral collection equipment. The instrument and method of analysis of samples for chromium content is also discussed.

Experimental Design

In order to achieve the experimental objectives of this thesis, a detailed methodology was devised. It was desired to collect inhalable particles into SLF. Several SLFs are used in the field so the most appropriate solution was selected. A cyclone was connected in series with an impinger filled with 30 ml of SLF. The paint samples were collected in a paint booth during typical spray painting operations.

Residence time of the paint particles in the SLF should mimic the residence time of foreign particles in the human lung. Mucociliary transport has been estimated from whole lung clearance curves. It is theorized there are two phase clearance curves: fast and slow. Fast clearance refers to tracheobronchial (conducting zone) clearance and is usually completed within 24 to 48 hours (Brain, 1994:120). Slow clearance refers to alveolar (respiratory zone) clearance. The potential contact time of a particle in the conducting zone of the lung is an area of focus so the fast clearance values were chosen as residence times: 24 and 48 hours. A third residence time was added to provide an

intermediate observation of chromium dissociation prior to the 24 hour residence time observation.

Atomic absorption spectrometry (AAS) with graphite furnace was used to analyze samples for chromium. Prior to analysis with the AAS, each sample had to be broken down to allow the chromium to atomize. To properly breakdown the collected samples for AAS chromium analysis, microwave digestion was performed on the samples.

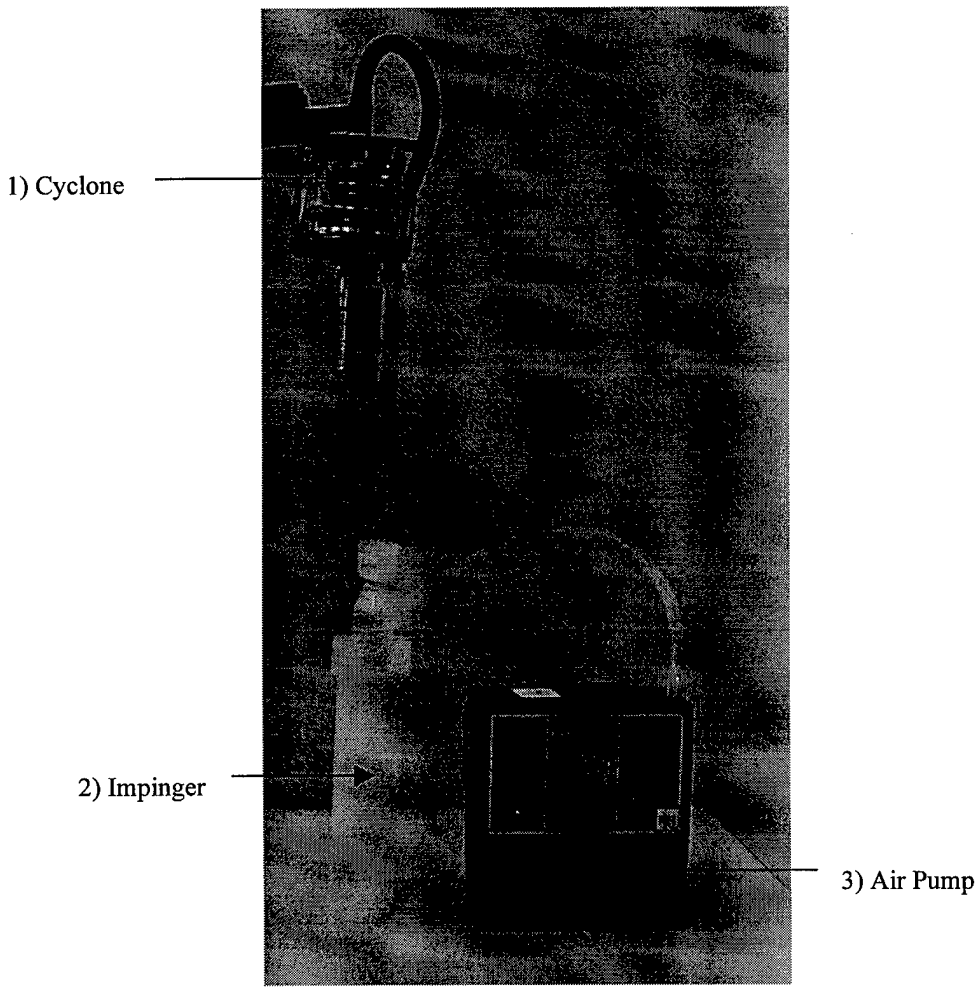


Figure 6. Pump, Impinger and Cyclone Configuration

The cyclone (1), impinger (2), and air pump (3) were connected by Teflon tubing as depicted in Figure 6. The pump and impinger were set in foam for stability during

sample collection. The cyclone was attached to a ring stand to suspend it approximately eight inches above the pump and impinger. This set-up was placed on a stand to elevate the cyclone height to approximately 2 feet during sample collection to match the level of the cyclones with the bottom edge of the test panel. Three set-ups were placed side-by-side to collect samples during spray painting operations simultaneously. The three cyclones were located within a 10" of each other.

The three sample collection devices were placed approximately one foot from the front of the paint booth and approximately ½ foot to the side of the easel. The painter's easel was 4 feet from the front of the paint booth and angled towards the collection devices at approximately 60 degrees with respect to the front wall. A CTIO technician painted a 24"x18" test panel on the easel. The panel sat on a ledge on the easel 3' off the ground. The placement of the sampling equipment tried to maximize the overspray collection. The sample collection setting is illustrated in Figure 7.

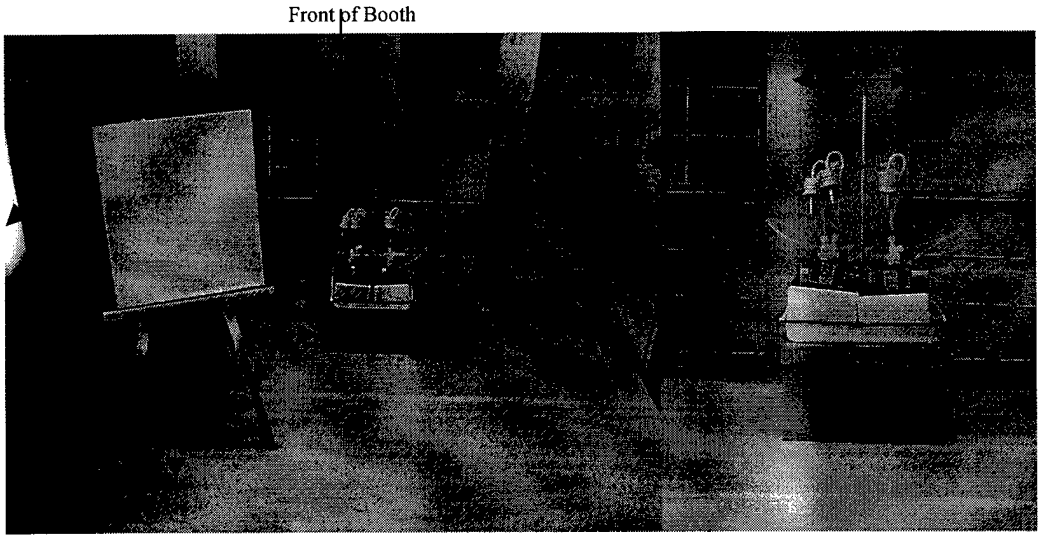


Figure 7. Paint Booth Set-up

The paint booth in which the samples were collected is humidity and temperature controlled. With a 99% confidence level, the temperature during sample collection was

76 ± 7 °F and the humidity during sample collection was 50 ± 7 %. This controlled environment booth was used to hold the temperature and humidity reasonably constant.

Simulated Lung Fluid.

There are two types of SLF in the literature: simulated surfactant lung fluid and interstitial lung fluid. The difference between simulated surfactant lung fluid and simulated interstitial lung fluid is surface active component (dipalmitoyl lecithin: DPL) in simulated surfactant lung fluid (Dennis, 1982:470). Biological fluids are difficult to recreate and lung fluid is no exception. Different variations were found in the literature but most, if not all, can be traced to Gamble's 1952 formula. SLF has been used to test solubility of uranium compounds (Cooke, 1974: 69; Duport, 1991:121), titanium tritide particles (Cheng, 1997:633), dissolution of fibers (Christensen, 1992:83; Mattson, 1994:87; Mattson, 1994:857), and dissolution of yellowcake- U_3O_8: a product of uranium milling used for fuel enhancement (Dennis, 1982:469; Eidson, 1984:151). SLF has also been varied with hydration states and applied to uranium trioxide (Ansoborlo, 1992:139). Some formulas include preservatives or proteins in addition to the standard salts to extend shelf life or more closely mimic the natural lung fluid. The process selected for this thesis involves filtrated ions to determine extent of strontium chromate dissociation and the use of proteins was determined to be unnecessary at this time. Proteins may result in foaming of solution, which would needlessly complicate this experiment. However, it is possible that proteins may play a role in affecting the breakdown of the paint matrix and therefore release of chromate.

The formulation selected for this experiment was devised by Fisher and Briant and is shown in Table 4 (Fisher, 1994: 264). There is a potential problem for precipitation of salts in the SLF formula due to high local concentrations when salts are initially added to solution (Moss, 1979: 447). Therefore, the Fisher SLF relied on a modified Gamble's solution with a 50% reduction in magnesium and calcium chloride salts to eliminate the precipitation problem (Fisher, 1994:264). The SLF was made in batches of 1 liter (L). SLF ingredients were added to 950 ml of ATSM Type II deionized (DI) water. Each ingredient was placed in a Daigger medium weigh boat and weighed using a Mettler scale. The ingredients were added sequentially in the order listed in the table below. When the desired mass of each ingredient was attained in the weigh boat, several drops of DI water were added to the boat to partially dissolve the ingredient. This enhanced the dissolution of each ingredient when added into the final volume and maximized product transfer from weigh boat to the final volume.

Table 4. Simulated Lung Fluid Ingredients

Description	Molecular Formula	Concentration in g/L ($\pm$ 0.1 mg)
Magnesium chloride	$MgCl_2 \cdot 6H_2O$	0.101
Sodium chloride	$NaCl$	6.019
Potassium chloride	KCl	0.298
Sodium phosphate	$Na_2HPO_4 \cdot 7H_2O$	0.268
Sodium sulfate	Na_2SO_4	0.071
Calcium chloride	$CaCl_2 \cdot 2H_2O$	0.184
Sodium acetate	$NaH_3C_2O_2 \cdot 3H_2O$	0.952
Sodium bicarbonate	$NaHCO_3$	2.604
Sodium citrate	$Na_3H_5C_6O_7 \cdot 2H_2O$	0.097

Cyclone.

The SKC 25 mm aluminum cyclone was chosen to select for particle size. A cyclone is a light-weight device commonly used in industrial hygiene (IH) field surveys to collect inhalable particles. An example cyclone is shown in Figure 8.

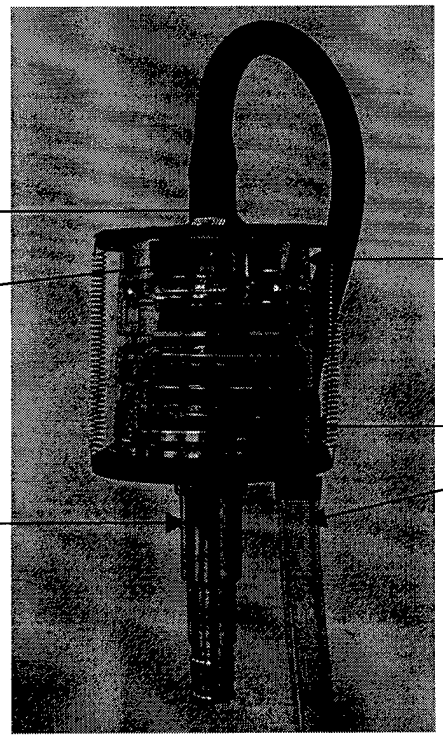


Figure 8. SKC Respirable Dust Cyclone

Cyclones are devices that select for particle size based on momentum. The cyclone was connected to a Gillian® GilAir 5 air pump. Air is drawn through the pump at a specific rate to achieve the desired particle size. The air enters the cyclone through an inlet port or slit (#3 in Figure 8) and is forced into a vortex. Larger, heavier particles will impact the sides of the cyclone and collect at the bottom of the cyclone. Lighter particles will remain in the air stream and travel towards the top of the cyclone. The outlet port (#1 in Figure 8) of the cyclone is connected to a three-piece plastic cassette (#4 in Figure 8),

which holds a filter located on the downstream side of the cassette (#2 in Figure 8) for sample collection. Teflon ¼" inside diameter tubing connects the outlet air to the Teflon midget impinger (#5 in Figure 8). Impingers are described later.

Airflow determines the particle size selected by the cyclone. The SKC aluminum cyclone is connected to an air pump drawing 1.9 liters per minute (lpm) airflow. This flowrate eliminates particles greater than 5 μm.

In this study, the filter was removed from the cassette allowing air to pass straight through the output opening to an additional device. Without the filter, the particles are free to travel towards the outlet opening. This unique alteration of device design may result in smaller particles actually collected in the SLF. Larger particles impacting the cassette prior to the outlet opening may affect the actual particle size that passes through the device.

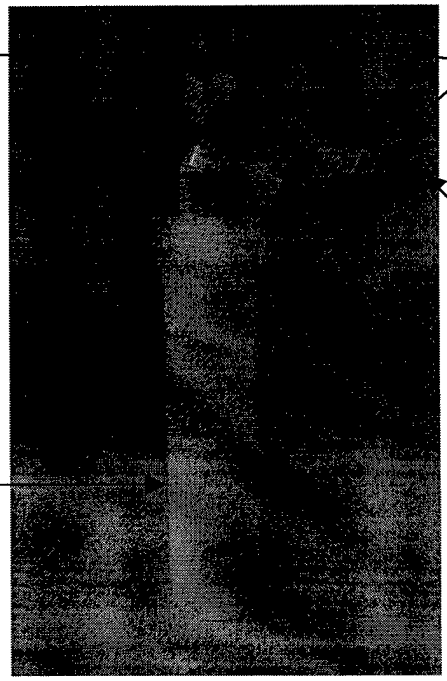


Figure 9. Midget Impinger

Midget Impinger.

Impingers were originally developed in the 20's by the American Bureau of Mines to collect particles larger than 0.75 μm in liquid medium for counting cells under a microscope. Today, impingers are mainly used to collect mists, sprays and vapors and airborne biological organisms (Lyons, 1992:S599). An impinger is a device that draws air through an impinger conducting tube (#1 in Figure 9), releasing the air at the bottom of a narrow cylinder that contains a fluid (#2 in Figure 9). The air bubbles through the fluid and some contaminant becomes trapped in the fluid while the air continues through airspace and tubing to air pump (#4 in Figure 9). The contaminant may not be thoroughly "scrubbed" by the air in the first impinger's fluid, so a second impinger is often connected in series to enhance the efficiency of contaminant capture. However, a second impinger was not used for two reasons. Due to low chromium concentrations in the first impinger, a second impinger would not provide added value. Additionally, the intent of this study was not to determine total chromium concentration. Instead, the starting chromium concentration would be compared to succeeding concentrations after filtering.

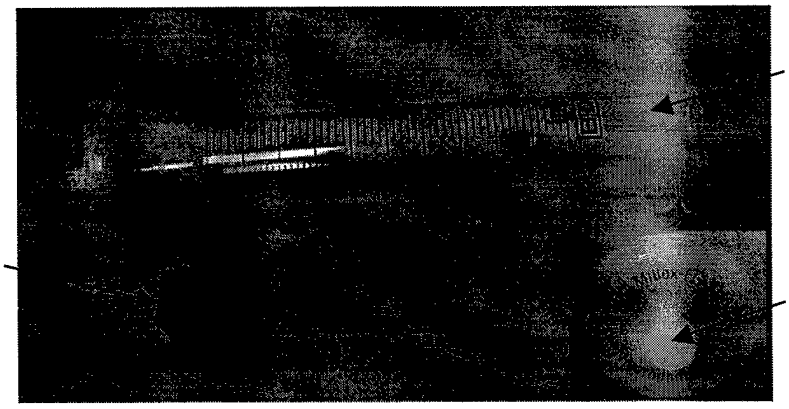


Figure 10. Millipore Filter and Beeton-Dickinson Syringe

Filter Selection.

A 0.2 μm filter (Figure 10) was chosen to discriminate between dissolved chromium ions and paint particles that may still harbor chromium. Although < 0.2 μm particles may pass through a 0.2 μm filter, it is assumed that the total mass contribution of such particles will not affect the results significantly.

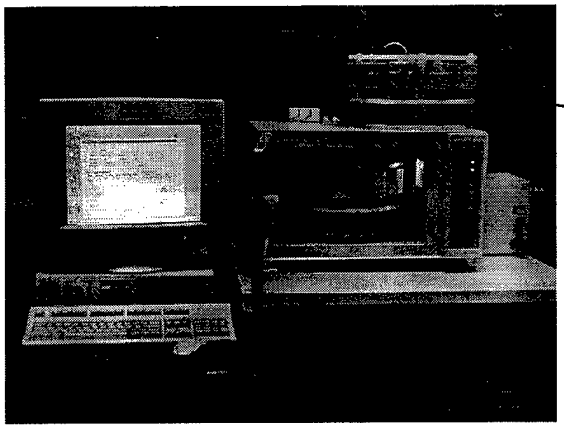
To determine whether ions were attracted or collected by the filter rather than passing through the pores, several different filters were tested to determine whether bias existed when analyzing filtered fluids for chromium. The goal of this process was to ensure that particles were not attracted to the filter and affecting the results. Two solutions of free strontium chromate were prepared. Three replicates of each solution were isolated and handled with the same procedures as the collected samples up to but not including digestion (discussed later). The analysis determined whether the filters were biasing the chromium concentrations. If the chromium concentrations in the filtered samples are not statistically different from the chromium concentration in the corresponding unfiltered samples, the results imply that the filter is not biasing the chromium concentration.

Sample Digestion.

Prior to analysis, particles in samples must be decomposed so that the analysis instrument can quantify chromium. Primer paints form polymerization links in a lattice structure. To analyze for chromium, the paint matrix must be broken down to release the chromium ions. Microwave digestion with nitric acid is used to decompose the paint. Due to the need for a strong oxidizing environment to breakdown paint particles,

microwave digestion is well suited for difficult materials like paint. The microwave also reduces analysis time and ensures a more complete destruction of the particles.

The OI Analytical Microwave Digestion System (Figure 11) was used to decompose the paint samples. No procedure exists for decomposing the paint samples collected for this thesis. However, microwave digestion methods for paint chips exist in EPA method 3050A and NIOSH Method 7300. The procedures for these methods were combined and modified for this thesis sample digestion. Preparation included diluting the sample with a volume of 70% nitric acid equal to the sample volume. The sample was digested at 50 psig for 5 minutes and 70 psig for 25 minutes.



Microwave carousel filled with digestion vessels

Figure 11. Digestion Microwave

Atomic Absorption Spectrometry.

Atomic Absorption Spectroscopy (AAS) is a measurement of the interaction of light with atoms. AAS uses a flame vaporizer or graphite furnace, to atomize an analyte within a sample. Due to expected low ppb chromium concentrations, the graphite furnace configuration was used to analyze samples. The flame vaporization configuration was used to determine chromium concentration for the solubility test.

A volume of 10 microliters (μl) of sample is injected into the furnace tube. The AAS method is presented in Table 4. First, the tube is heated by passing current through the tube. In the drying step (step 1), the sample is heated to remove all water. The drying step must be done slowly to avoid splattering and consequently loss of sample. Argon gas flows to remove evaporated solvent. The charring and pyrolysis steps are steps 2 and 3. These steps volatilize inorganic and organic matrix components leaving the analyte in a less complex matrix. Steps 2 and 3 further remove undesired components of the sample but are completed at a temperature low enough to avoid volatizing the analyte of interest. Step 4 is atomization. By further increasing the temperature, atomic vapor is created from the sample which absorbs light directly proportional with the analyte concentration. When the argon flow is stopped, the analyte absorbance is recorded. The last step (5) is the cleaning step. This step raises the temperature again and forces gas through the tube to clean any residual substance left in the tube, preparing it for the next sample (Beaty and Kerber, 1993: 5.7-5.9). Care was taken when developing the method parameters to maximize absorbance and minimize incomplete charring which produces smoke during atomize stage potentially producing erroneous results.

Table 5. Atomic Absorption Method Parameters

Parameters → / Steps ↓	Final Temp (°C)	Ramp Time (s)	Hold Time (s)	Gas	Read Signal
1: Drying	80	5.0	10.0	Argon	Off
2: Charing	130	30.0	10.0	Argon	Off
3: Pyrolysis	1400	15.0	15.0	Argon	Off
4: Atomization	2500	1.4	1.6	None	On
5: Clean	2700	0.5	1.5	Argon	Off

During the atomization step, some of the chromium atoms are thermally excited by the heat energy. These ground state atoms are able to absorb radiation emitted by the source. The source is typically a hollow-cathode lamp made of the same material as the analyte of interest. Transmittance (T) is defined as the amount of light transmitted (P) through the cloud of excited atoms divided by the baseline (no sample) light intensity (P_o). Beer's Law is used to relate the transmittance (T), the path length through the sample (b), the concentration of chromium atomic vapor in the flame/cloud (c), and absorptivity (a) for a single wavelength. Absorbance (A) which is the instrumental output is the negative log of transmittance. The two described forms of Beer's Law are shown below (Christian, 1994:414).

$$T = \frac{P}{P_o} = 10^{-abc} \qquad A = -\log T = abc$$

The optimal range of the AAS with platform stabilized graphite furnace is roughly 10-650 ppb for chromium with autodilutions. (Christian, 1994:467-480 and McGowin, 1999).

Modifiers (typically salts) are commonly added to samples to retain the analyte of interest in the tube until the atomization step. Due to the high content of salts in the SLF,

a modifier was not necessary. Chromium has several absorption wavelengths. The AAS settings used were 357.9 nm wavelength with a 0.2 nm slit width and lamp current of 6.0 mA.

Although the graphite furnace is described above in detail, the flame method follows the same principles. However, the sample is aspirated through an air-acelytene flame then compared to the reference. Both methods have an autosampler that can introduce samples automatically. Additionally, the graphite furnace autosampler can create multiple concentration calibration standards from a stock sample. The spectrometer with both auto sampler attachments is pictured in Figure 12. A close up of the graphite furnace auto sampler PAL 3000 is in Figure 13.

Figure 12. GBC Atomic Absorption Spectrometer

Figure 13. Graphite Furnace PAL 3000

Strontium Chromate Saturation Limit in SLF.

It was useful to determine the saturation limit of strontium chromate in SLF. The solubility of strontium chromate in SLF was compared to the solubility of strontium chromate in water. This provided insight into the saturation point for strontium chromate in SLF. It was important to know at what point the strontium chromate product in the SLF would precipitate. Over saturating the SLF could affect the chromium concentration comparison between the filtered and unfiltered samples.

To determine the solubility of strontium chromate in the SLF, the *Water Solubility* test from the Organization for Economic Co-operation and Development Environmental Fate Guideline for Testing of Chemicals was referenced. This organization defines

standards for determining solubility values. The solubility of strontium chromate in water is 1,200 ppm at 15 °C and is 30,000 ppm at 100 °C (Weast, 1985: B-147). Three flasks containing 200 ml of SLF were spiked with an abundance of free strontium chromate. The flasks were heated in a water bath at 45 °C for 48 hours. The flasks were transferred to a 37 °C incubator. After 72 hours, the samples were spun in an International Equipment Company centrifuge model 428 for 10 minutes at 3300 rpm. The centrifuged supernatant was analyzed by flame atomic absorption spectrometry. Ten replicates were done on each sample. The results were averaged to estimate the concentration of chromium as 61.6 ppm. Since chromium comprises 25% of strontium chromate and assuming all chromium present was provided by the free strontium chromate, the solubility of strontium chromate (as chromium) in SLF at 37 °C was determined to be approximately 61.6 ± 0.25 ppm (240 ppm). The addition of the SLF salts reduces the saturation limit of strontium chromate (as chromium) by approximately 20%.

Procedures

Equipment Preparation.

Prior to sample collection, the three impingers from the three set-ups were cleaned with DI water with 7% nitric acid and rinsed with DI water three times. 30 ml of SLF were added to the midget impingers. After preparing the impingers, the GilAir pumps were calibrated to approximately 1.9 lpm using a Gilibrator model # 800286.

Sample Collection.

A laboratory ring stand and accompanying clamps positioned the cyclones at a constant height during the sample collection period. Immediately prior to sample collection, the entire set-up was encased in plastic bags up to but not including the cyclone. Care was taken to ensure that the cyclone slit intake was not affected by the plastic covering.

The pumps were started less than a minute before the paint technician began painting. When painting operations ceased the pumps were turned off. The stop time occurred less than a minute after painting operations had ceased. Total sample time was recorded. The outer surfaces of the cyclone were cleaned with methyl ethyl ketone (MEK) between each sample. After sample collection, the GilAir pumps were recalibrated to check flow rate. If the post calibration flow rate significantly differed from the pre calibration flow rate, the recorded flow rate was an average of pre and post calibration flow rates. Samples were transferred from Teflon impingers to 30 ml Nalgene high density polyethylene (HDPE) bottles and labeled.

Sample Residence Time.

Residence times of 6, 24 and 48 hours were selected to test if time influenced dissolution of chromate ions from the paint particles. To determine whether residence time affected the dissociation of strontium chromate from the sample, the collected samples were held at body temperature (37°C) for the designated times in an Imperial III Labline incubator. Once each residence time was reached, 7 ml of the sample was pipetted into a Becton-Dickinson 10 ml latex-free syringe equipped with a Millipore

Millex® non-sterile hydrophobic fluoropore (PFTE) 0.2 μm. Each sample was slowly pushed through the filter into a labeled 30 ml Nalgene HDPE bottle. Each sample was preserved with 100 μl of 7% Nitric acid. 100 μl of 7% nitric acid was required to lower the pH of ~6.2 ml of sample to pH ≤ 2. To standardize filtered and unfiltered sample volumes, 6.2 ml of unfiltered sample was pipetted into its HDPE bottle.

Sample Analysis.

GBC Avanta Atomic Absorption Spectrometer with autosampler was used to quantify chromium concentration in each sample. The automix function was used to create dilutions from a stock concentration for calibration standards. A standard four point calibration curve method was used.

A 1000 ppm hexavalent chromium (Environmental Resource Associates lot # 08098.1) standard with water containing 7% nitric acid for dilution was used to create calibration standards. The nitric acid keeps the chromium in solution and hinders chromium sorbance to the container walls. A stock of 100 ppb was prepared to be auto-mixed into 10, 25, 50 and 70 ppb chromium concentrations. Stocks of 10, 25 and 50 ppm chromium concentrations were created for the flame spectrometry. A linear least squares regression analysis was used to create the calibration curve. A regression factor (R^2) of 0.9825 was required for acceptance.

Determining the instrument limit of detection (LOD) can be accomplished in several ways. The method chosen required analyzing several blank samples and calculating the standard deviation. The concentration that represents a signal equal to three times that calculated standard deviation is the detection limit (Christian, 1994:53).

The calibration blanks served as background concentration. The ten calibration curve LODs were averaged. The limit of detection was 2.85 $\pm$ 1.64 ppb for the graphite furnace configuration.

Several quality standard practices were implemented. Each sample was analyzed at least three times and the results averaged. Ideally, the relative standard deviation (RSD) was $\leq$ 5% among the three replicates. Mainly due to the low concentration of many samples, the RSD was larger than desired. If the RSD was significantly greater than 5% and the sample concentration was high, the result was suspect and analyzed again. For every 10 samples, a High Purity Standards (HPS) Certified Reference material 20 ppb check sample was analyzed (Lot # 812708 Exp N/A and Lot # 927704 Exp Jan 01). If the check sample was $\pm$ 20%, the system was assumed to be acceptable. The system was rescaled if the check sample was outside the 20% range. The rescale function used a 40 ppb calibration standard. If the 40 ppb calibration concentration was outside the accepted 20%, the calibration curve was shifted by the percent change from the 40 ppb calibration standard absorbance.

Statistical Analysis

Two statistical testing paths were taken to answer two thesis questions. One research objective was to determine if residence time influences the dissociation of strontium chromate in SLF. If residence time influenced the dissociation of strontium chromate in SLF, a mathematical relationship exists between the chromium concentrations of the three grouped filtered samples. Determining the answer to this research goal will be the first statistical test.

To meet the above stated research objective, it needed to be determined if there was a mathematical relationship between the chromium concentrations of each three grouped filtered samples. If a mathematical relationship existed, it would be nondeterministic. Potential nondeterministic relationships are determined with regression analysis (Devore, 1995:474). Each group of three filtered samples were scatter plotted and a regression line fit to the data. The regression lines of the twenty-seven samples were observed for commonality. If there was no common statistically significant trend among the regression lines, so additional analysis was not required. The second line of statistical testing sought to answer the thesis objective.

The objective of this thesis was to determine if the dissociation of chromate in SLF was hindered when bound in paint particles. A hindrance was defined as a decrease in chromium concentration of a filtered sample compared to its respective unfiltered samples. A Dunnett's Test was conducted to determine if a statistical difference existed between the unfiltered and filtered chromium concentration means.

A Dunnett's test compares the mean of experimental data to the mean of the control data. The Dunnett's test allows one to control the alpha value (rejecting the null hypothesis when it is true) (Sheskin, 1997:340). The Dunnett's test identified if the means of the chromium concentration of the filtered samples significantly differed from the mean chromium concentration of the unfiltered sample.

Experimental Measurements

Paint Sample Results

All raw data and calibration curve data are found in Appendix A.

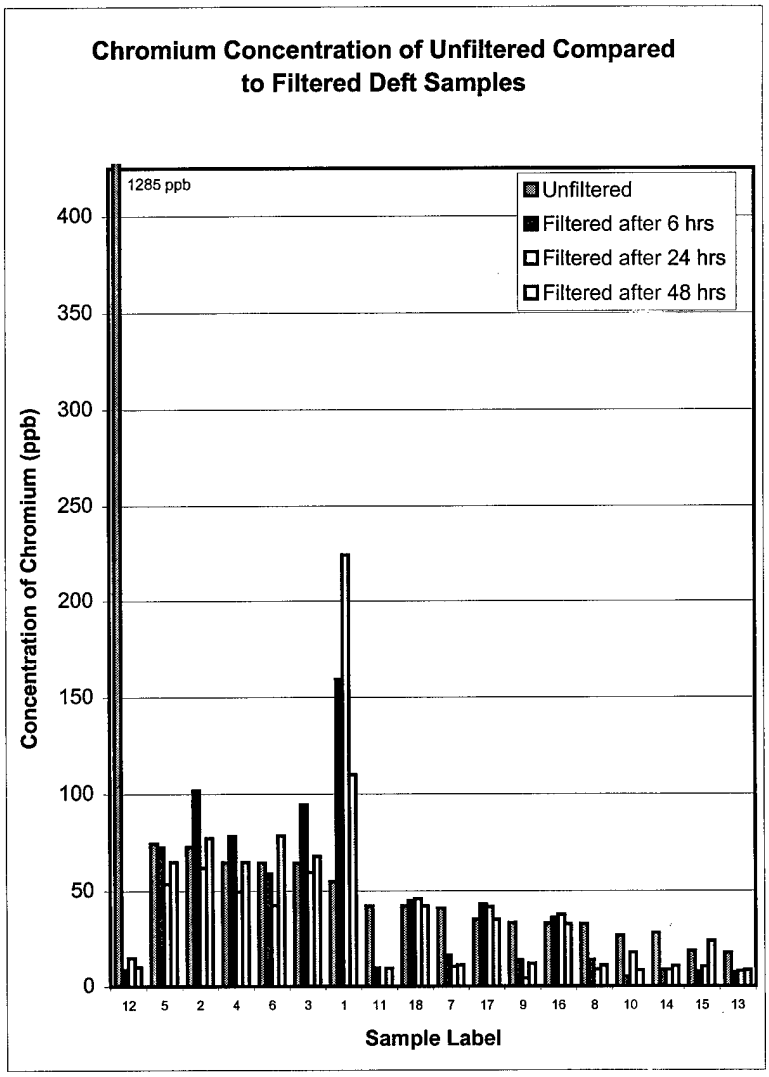


Figure 14. Chromium Concentration of Unfiltered Compared to Filtered Deft Samples

The Deft manufacturer data is presented in Figure 14. Figure 14 shows each unfiltered sample chromium concentration side-by-side with the chromium concentrations of its three respective filtered samples. Many samples appear to have a reduction in chromium concentration when comparing unfiltered to filtered. Several samples appear to have no difference between the unfiltered chromium concentration and the corresponding filtered concentrations. There are a few anomalies where filtered chromium concentrations are greater than unfiltered chromium concentrations.

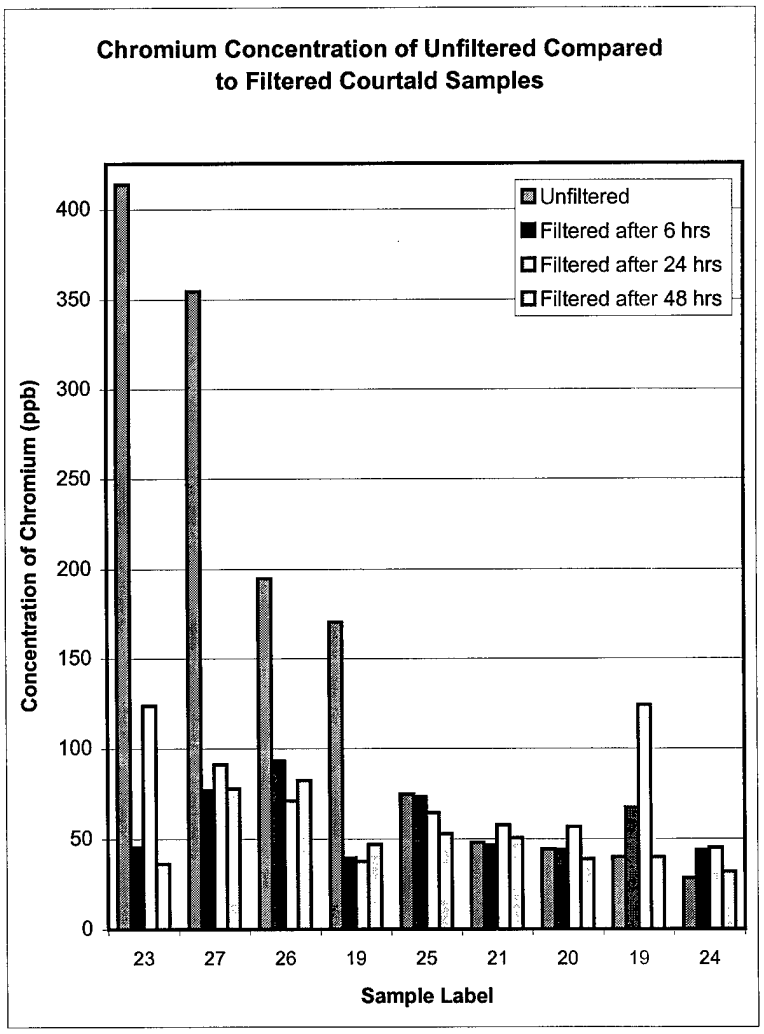


Figure 15. Chromium Concentration of Unfiltered Compared to Filtered Courtalds Samples

The Courtalds manufacturer data is shown in Figure 15. When the unfiltered (initial) chromium concentration samples are 150 ppb or greater, there appears to be a large percentage reduction in filtered chromium concentration. However, when the initial chromium concentration is 50 ppb or below, there is not a noteworthy reduction in filtered chromium concentration.

Paint Sample Statistical Results

To achieve the first research objective, it was desirable to see if residence time had an influence on the dissociation of strontium chromate in SLF. Each set of three filtered samples (6 hr, 24 hr and 48 hr residence times) were scatter plotted and a linear regression line fit to the data. No commonalities were noticed among the regression lines. The lack of an apparent trend among samples implies that residence time does not influence chromium concentration in SLF.

To achieve the thesis objective it was necessary to determine the relationship between the chromium concentration of the filtered samples and the chromium concentration of their respective unfiltered sample. This was conducted using a Dunnett's Test.

The Dunnett's test is a multiple comparison of means with a confidence interval of 95%. The Dunnett's test compares the difference between the control mean and sample mean with the confidence interval about zero. If the confidence interval does not include zero and both end points are negative, the sample mean is statistically smaller than the control mean implying a Type 1 population. If the confidence interval does include zero so one end point is negative and one is positive, the sample mean is not

statistically different from the control mean implying to a Type II population. If the confidence interval does not include zero and both end points are positive, the sample mean is statistically greater than the control mean implying a Type III population. In this thesis, the sample means are the mean chromium concentrations of the filtered samples and the control means are the mean chromium concentration of the unfiltered samples. Detailed Dunnett's test theory and procedures are outlined in Appendix B. Figure 16 illustrates Type I, Type II and Type III populations.

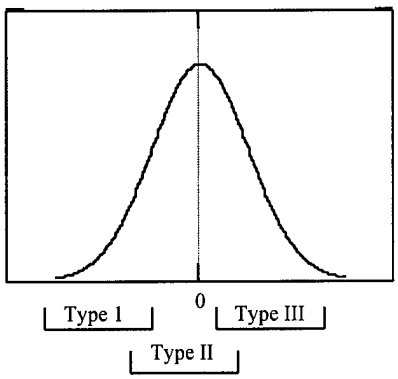


Figure 16. Statistical Category Representations

To make the statistical results more meaningful an assumption was made. If two of three filtered samples fell into a population Type as defined in the previous paragraph, the third sample is grouped into the same sample population as the two filtered samples. If all three filtered samples fell into different population types, the filtered samples were classified as Type II.

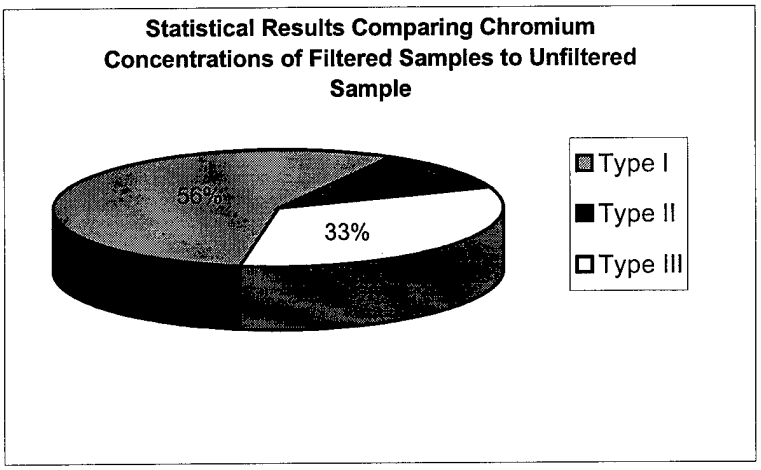


Figure 17. Statistical Results Comparing Chromium Concentration of Filtered Samples to Unfiltered Sample

The results of all the samples were compiled and shown in Figure 17. 56 % (15/27) of the samples resulted in Type I populations. 33 % (9/27) of the samples fell into Type II populations. 11% (3/27) of the samples resulted in Type III populations.

Manufacturer Specific Data

Deft data

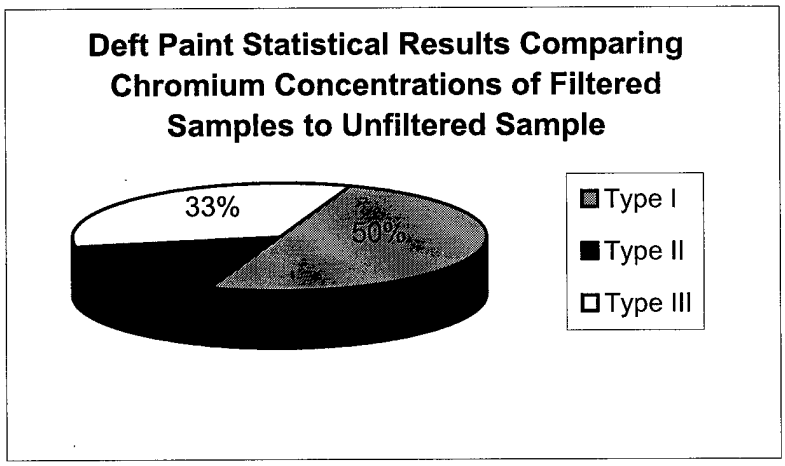


Figure 18. Deft Qualitative Statistical Results Comparing Chromium Concentration of Grouped Filtered to Unfiltered

The results of the Deft data evaluation are as follows. 50% (9/18) samples fell into Type I populations. 33 % (6/18) of the Deft samples were classified as Type II populations. 17% (3/18) of the samples were categorized as Type III populations. Figure 18 pictorially represents the population category segregation using the Deft data results.

Courtalds data.

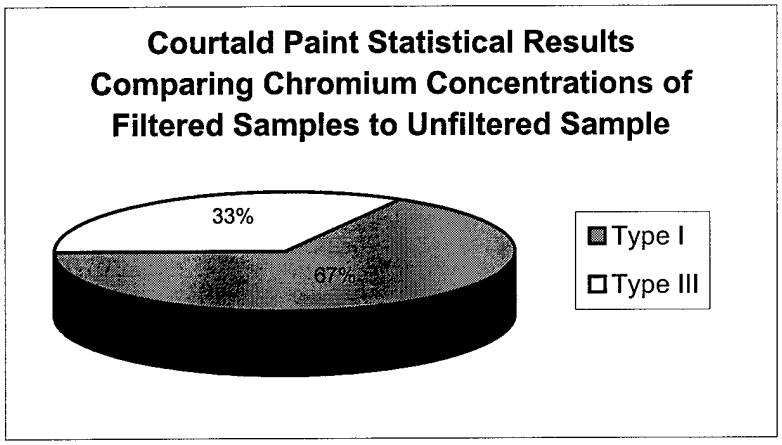


Figure 19. Courtalds Qualitative Statistical Results Comparing Chromium Concentration of Grouped Filtered to Unfiltered

The results of the Courtalds data evaluation are as follows. Figure 19 shows 67 % (6/9) of the Courtalds samples were classified as Type I populations. 33% (3/9) Courtalds samples were categorized as Type III populations.

Chromium Concentration Bias Testing.

The objective of the following tests was to check for potential chromium concentration bias. A test was conducted to determine whether the filtering process biased the chromium results. Additionally, a test was conducted to see if other chromium sources were potentially contributing to the chromium concentration of the paint particle samples.

Filter Bias Testing Results.

The filter bias test was performed to identify whether the 0.2 μm filtering step had an influence on the chromium concentration results in SLF. Two samples were spiked with free strontium chromate, one with 700 ppb chromium and one with 150 ppb chromium. The spiked samples were treated with the same filtering, preservation, digestion and analysis as paint samples. Statistical analysis was performed on the chromium concentration of the samples. Figure 20 shows the results of the filter bias testing.

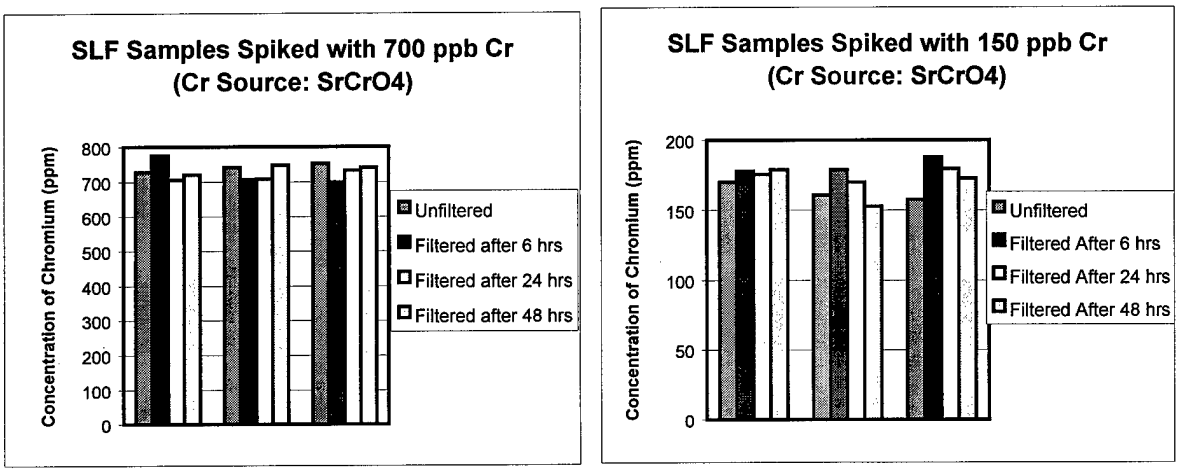


Figure 20. SLF Samples Spiked with 700 and 150 ppb Cr

Visually, the unfiltered treatment compared to the filtered treatment of both ~700 and ~150 ppb chromium concentrations appear to be essentially the same. The Dunnett's test was used to compare each unfiltered sample with each of three respective filtered samples. All 700 ppb samples fell in to Type II. The 150 ppb samples were Type III. It seems unusual that the chromium concentration of the filtered samples were shown to be consistently statistically greater than the chromium concentration of the unfiltered sample. However, this discrepancy is probably due to the relative concentration difference between the 150 and 700 ppb. For the purpose of this thesis, the values imply

the filter has no effect on chromium concentration of unfiltered compared to filtered samples.

Quality Testing.

Chromium was analyzed in blanks and in sample containers to test for chromium additions from unknown sources. Blanks were prepared using only SLF and processed identically to all other samples and then analyzed. The averaged concentration of the straight SLF samples was 6.4 ± 5.1 ppb. This overlaps with the detection limit of 2.85 ± 4.92 (99% confidence). The lack of detectable chromium in the straight SLF samples implies all chromium concentrations from collected samples originate from paint overspray.

Another concern affecting the accuracy of chromium concentration in collected samples is chromium attracted to the sample container vessel walls. If the chromium adhered to the container walls, resulting chromium concentrations would be lower than true chromium concentrations. To test the sample container for residual chromium, two samples bottles were filled with 7% nitric acid and allowed to sit overnight while the paint particle sample was digested then stored in the Teflon lined digestion vessel. The chromium results were 1.8 ± 2.4 ppb indicating that all chromium remained in solution.

Results Summary

The data suggests that primer paint has a hindering influence on chromate dissociation in SLF although conflicting data prevents a firm conclusion. The higher percentage of Type I population classifications implies that the chromate was present in the unfiltered samples but not present in the filtered samples. This could mean that the primer paint particle binds the chromium and does not allow it to dissociate in SLF. If

true, this hindering phenomenon could affect the availability of the chromium for items in contact with the chromium in the paint particles.

All data points were included in interpretation; however, some filtered sample chromium concentrations were greater than the unfiltered chromium concentration. It is impractical that a filtered sample would have greater chromium concentration than the unfiltered control sample. Such results could be explained by potential sources of error as discussed in the next section.

Potential Sources of Error

There are several potential sources of error. First, the microwave digestion method may have less recovery of chromium when compared to recovery from hot plate digestion (Kingston, 1992:25). On a small experiment scale, the hot plate method introduces more chances for random error than the more automated microwave method. Due to this potential difference in the random error, it is hypothesized that the microwave chromium recovery is better than the hot plate chromium recovery.

Additionally, the paint particles may not have fully digested. If the paint particles were not fully digested, it is possible that digestion may not have been uniform throughout the digestion period. Chromium concentrations reported may not be accurate. To validate the digestion method, a known amount of primer paint could be digested and analyzed. Percent recovery of chromium could then be determined.

All sources of error cannot be determined and/or quantified. It is assumed that by reporting all results with 99% confidence (three standard deviations), the majority of error is incorporated.

Saturation Limit Results

The chromium concentration of the samples may have been biased if the chromium concentration approached the saturation limit of strontium chromate (as chromium) in SLF. The chromium concentration of the samples (1.2 - 1285 ppb) did not approach the saturation limit (240,000 ppb) so it is unlikely that the chromium concentrations were affected.

The temperature of the samples could affect chromium concentration due to saturation limits. The methodology employed kept samples at 37°C only prior to filtering. After filtration the samples were stored at 25°C. Temperature affects solubility. It may be beneficial to incorporate methods to store samples at all stages at 37°C.

Microscope Results.

Twelve samples were viewed under an oil immersion microscope. Calibrated 9.65 μm microspheres were used as a reference while each sample was viewed under the microscope. This side-by-side observation enabled a direct comparison between particle size and the calibrated mircrospheres. Observation of the particles under the microscope revealed many particles much smaller than the microspheres. It appeared the majority of particles in the samples were ≤ 5 μm. These smaller particles appeared spherical. A few particles of 10-30 μm were also observed. These larger particles were random conglomerations with no identifiable shape. The microscope observations confirmed the desired collection of particles ≤ 5 μm as most particles appeared below the threshold.

Conclusions

Some interesting trends were observed in the results. Residence time appears to have little influence on dissociation. Some of the data, in particular the Courtalds data, suggests some reduction in dissociation of chromium between unfiltered and filtered samples. This may indicate a hindering of chromium dissociation when bound in a paint particle.

An interesting observation is the distinct difference in unfiltered (initial) chromium concentration between the manufacturers. The Deft and Courtalds samples were collected for the same amount of time. Most Deft unfiltered samples ranged from 25-75 ppb while approximately half the Courtalds samples ranged from 170-410 ppb. The Material Safety Data Sheet (MSDS) states that the Deft solids component is 25% strontium chromate and the Courtalds solids component is 30 % strontium chromate. Deft and Courtalds solids components are mixed in a 3:1 ratio with the catalyst. Therefore, as each solids component comprises 75% of the total paint volume, Deft paint is 18.75% strontium chromate and Courtalds paint is 22.5% strontium chromate. The overall higher chromium concentrations found in unfiltered Courtalds samples are consistent with the greater strontium chromate content as listed in the MSDS. However, the 4% difference in overall strontium chromate content in the Courtalds paint is inconsistent with the difference in Deft and Courtalds unfiltered chromium concentrations. This difference may be due to a difference in the manufacturer paint formulation. Greater differences in chromium concentrations between unfiltered and

filtered samples in Courtalds samples may indicate that Courtalds' formulation results in a stronger hindrance of chromium dissociation. Alternatively, the low initial chromium concentrations may be too low for the equipment to reliably detect a difference in concentration.

Another theory for the difference in unfiltered chromium concentrations is the transfer efficiency of the paint to the painting surface. A painter with high transfer efficiency will transfer a larger percentage of paint to the aircraft surface when compared to a less efficient painter. This difference in painter technique could account for a small portion of the difference in unfiltered paint concentration.

The chromium content of a paint particle may be dependent on the size of particle. The larger paint particles should reach the paint surface while the smaller particles would be most likely to be carried by air currents away from the paint surface. A bias in the chromium content due to particle size may account for the differing initial chromium concentrations in the Deft and Courtald samples.

Different manufacturers of paints may produce different paint particle size distributions when expelled through identical guns with identical parameters. This particle size disparity may influence the chromium content. It is theorized that particle size influences the chromium content. If the particle production varies by manufacturer based on formulation differences, the chromium content could vary.

There appears to be a difference between the Deft and Courtalds dissociation. The Courtalds paint composition seems to have a hindering affect of dissociation of chromium. The majority of the unfiltered Courtalds samples had greater chromium concentrations than the filtered samples.

Follow-on Research

The microwave method was fashioned after the EPA method for analyzing lead chips. Further research could take given quantities of paint mixed with its catalyst (implying known chromium concentration) and analyze the samples. Comparing the results to the expected chromium content would determine the effectiveness of the microwave method used to decompose paint particles.

Several aspects to further research would be the efficiency of particle collection. One could follow standard guidelines to properly characterize the particle size collected in the equipment set-up. Analysis of the particle size would greatly enhance understanding.

The particles observed indicated a very large proportion of expected size particles (< 5 μm). In addition, there were some larger sized particles. These larger particles could be particles passed through the instrumentation or agglomeration of smaller particles after collection into SLF. The agglomeration of particles may be due to several phenomena. The particles could be clustered due to the polymerization of paint particles from the paint gun. Alternatively, the smaller particles could be electrostatically attracted. Once delivered to SLF, the charged particles could attract then polymerize to form larger particles.

Increasing the number of samples collected will improve the quality and reliability of the data and conclusions. A larger number of samples will allow improved statistical analysis and greater certainty when discerning potential trends. Only basic observations can be determined from twenty-seven samples (Nine of Courtalds and 18 of Deft).

Dissociation for compounds quite often varies with pH, temperature, bubbled oxygen, and other fluid parameters. Holding other variables constant while varying the previously mentioned parameters will lead future research to which parameters are most important in dissociation. Those parameters were outside the scope of this thesis but may be of interest in future research.

This thesis addresses the dissolution of chromate when bound in a paint matrix. The indirect effect of dissolution of chromate when bound in paint is the effect on the human body. An endeavor to determine the effect on the human body would be an inhalation study using research animals. The most important parameter would be to introduce manufacturer specific paint overspray to the test subjects. From this, damage to the lung and potential cancer effects could be investigated. Moreover, analysis of other organs will indicate the fate and transport of chromium through the various tissues.

Isolation of the chromium ions was attempted using a 0.2 μm filter. Centrifuging the samples may improve the capture of chromium ions in solution. A possible improvement in the chromium ion extraction method would be to centrifuge each filtered sample prior to analysis. Analyzing the supernatant should more accurately capture the chromium dissociation in a fluid.

One parameter that could be important is consistent temperature of the samples. If the samples are centrifuged rather than filtered to isolate the ions, it might be important to centrifuge at 37 °C. If the samples are not kept at 37 °C while centrifuging, the sample could cool enough to precipitate chromium from the supernatant. The precipitation could affect the analyzed chromium concentrations and thus skew comparisons made between unfiltered (uncentrifuged) and filtered (centrifuged) samples. Additionally, storing the

samples at 37 °C after centrifuging and prior to AAS may be important for the same reasons as listed previously. It may be fruitful to centrifuge and hold samples awaiting analysis within a controlled climate.

Alternatively, an ingestion study on rats could be performed. Particles mucociliated from the lungs are eventually either expectorated or ingested. Future research could examine how the digestive tract affects the absorption and movement of chromium through living tissues.

Availability of hexavalent chromium to the industrial worker is of great concern. Greater depth of follow-on research will be key to determining the human hazards associated with chromium in paint overspray.

APPENDIX A: Filtering Data, Calibration Curves and Raw Data

The Filtering Data table relates the data labels in the thesis document to the calibration curve and raw data found in the raw data tables. It identifies the label assigned to the four grouped samples (1 unfiltered and three filtered).

Table 6. Filtering Data with Raw Data Identification

			Sample Filtered After 6 hours			**Sample Filtered After 24 hours**			**Sample Filtered After 48 hours**			**Unfiltered Sample Data**	
Thesis Document Label	Sample ID	Collection Time min	Sample ID	Filter Vol ml	Nitric Vol ml	Sample ID	Filter Vol ml	Nitric Vol ml	Sample ID	Filter Vol ml	Nitric Vol ml	Analyzed Vol ml	Nitric Vol ml
1	102101	0:24:41	102104	2.5	0.1	102204	2	0.1	102307	2	0.1	6.2	0.1
2	102102	0:24:50	102105	7	0.1	102205	7	0.1	102308	7	0.1	6.2	0.1
3	102103	0:25:00	102106	7	0.1	102206	7	0.1	102309	7	0.1	6.2	0.1
4	102107	0:22:42	102110	7	0.1	102214	7	0.1	102313	7	0.1	6.2	0.1
5	102108	0:22:27	102111	7	0.1	102215	7	0.1	102314	7	0.1	6.2	0.1
6	102109	0:22:27	102112	7	0.1	102216	7	0.1	102315	7	0.1	6.2	0.1
7	102201	0:23:03	102211	7	0.1	102301	7	0.1	102401	7	0.1	6.2	0.1
8	102202	0:23:00	102212	7	0.1	102302	7	0.1	102402	7	0.1	6.2	0.1
9	102203	0:23:07	102213	7	0.1	102303	7	0.1	102403	7	0.1	6.2	0.1
10	102208	0:30:58	102217	7	0.1	102310	7	0.1	102404	7	0.1	6.2	0.1
11	102209	0:31:01	102218	7	0.1	102311	7	0.1	102405	7	0.1	6.2	0.1
12	102210	0:31:00	102219	7	0.1	102312	7	0.1	102406	7	0.1	6.2	0.1
19	102501	0:25:36	102504	7	0.1	102604	7	0.1	102712	7	0.1	6.2	0.1
20	102502	0:25:38	102505	7	0.1	102605	7	0.1	102713	7	0.1	6.2	0.1
21	102503	0:25:41	102506	7	0.1	102606	7	0.1	102714	7	0.1	6.2	0.1
22	102601	0:28:52	102607	7	0.1	102705	7	0.1	102804	7	0.1	6.2	0.1
23	102602	0:28:54	102608	7	0.1	102706	7	0.1	102805	7	0.1	6.2	0.1
24	102603	0:28:58	102609	7	0.1	102707	7	0.1	102806	7	0.1	6.2	0.1
25	102701	0:27:45	102708	7	0.1	102801	7	0.1	102901	7	0.1	6.2	0.1
26	102702	0:27:52	102709	7	0.1	102802	7	0.1	102902	7	0.1	6.2	0.1
27	102703	0:27:57	102710	7	0.1	102803	7	0.1	102903	7	0.1	6.2	0.1
13	112004	0:30:10	111804	7	0.1	111901	7	0.1	112001	7	0.1	6.2	0.1
14	112005	0:30:15	111805	7	0.1	111902	7	0.1	112002	7	0.1	6.2	0.1
15	112006	0:30:30	111806	7	0.1	111903	7	0.1	112003	7	0.1	6.2	0.1
16	112404	0:49:05	112204	7	0.1	112301	7	0.1	112401	7	0.1	6.2	0.1
17	112405	0:48:55	112205	7	0.1	112302	7	0.1	112402	7	0.1	6.2	0.1
18	112406	0:49:00	112206	7	0.1	112303	7	0.1	112403	7	0.1	6.2	0.1
700ppb	112504	N/A	112310	7	0.1	112407	7	0.1	112501	7	0.1	6.2	0.1
700ppb	112505	N/A	112311	7	0.1	112408	7	0.1	112502	7	0.1	6.2	0.1
700ppb	112506	N/A	112312	7	0.1	112409	7	0.1	112503	7	0.1	6.2	0.1
150ppb	112510	N/A	112313	7	0.1	112410	7	0.1	112507	7	0.1	6.2	0.1
150ppb	112511	N/A	112314	7	0.1	112411	7	0.1	112508	7	0.1	6.2	0.1
150ppb	112512	N/A	112315	7	0.1	112412	7	0.1	112509	7	0.1	6.2	0.1

ID = Identification Vol = Volume Sample ID can be used in Table 7 to find raw chromium concentration

The calibration curve data tables that follow include sample concentration (Conc), mean absorbance (Mean Abs), absorbance replicates (Abs Reps), the slope and intercept of the regression line as well as the regression factor (R^2), the standard deviation of the replicates (St Dev) and the percent relative standard deviation (%RSD). The sample data tables include calibration curve categories as well as concentration replicates (Conc Reps) and a standard deviation associated with the concentration replicates. The slope and intercept use the calibration standards absorbances to create a calibration curve. The regression factor represents how closely the regression line fits the calibration standards and indicates the error associated with using the identified slope and intercept. Concentrations are calculated using the recorded absorbance and the calibration curve. Dilution values indicate whether the sample was diluted prior to analysis and whether it was executed automatically by the instrument or manually by the experimenter.

Table 7. Calibration Curves and Corresponding Raw Data

Sample Label	Conc ppb	%RSD	Mean Abs	Abs Reps			StDev
Cal Blank	-----	61.195	0.004	0.009	-0.002	0.004	0.006
Standard 1	10	3.903	0.167	0.168	0.16	0.173	0.007
Standard 2	25	2.305	0.335	0.337	0.341	0.326	0.008
Standard 3	40	1.233	0.684	0.693	0.683	0.676	0.009
Standard 4	55	0.513	0.852	0.85	0.857	0.849	0.004
Standard 5	70	0.454	1.167	1.165	1.163	1.173	0.005

slope	58.856
intercept	2.277
R^2 =	0.988

Sample Label	Dilution		Conc ppb	%RSD	Mean Abs	Abs Reps			StDev	Conc Rep			StDev
	A	M											
Sample Blank	1	1	2.081	208.167	-0.003	-0.001	-0.004	-0.005	0.002	2.218	2.042	1.983	2.400
101701	1	1	4.867	17.256	0.044	0.038	0.043	0.051	0.007	4.514	4.808	5.279	2.663
Sample Blank	1	1	2.257	146.487	0.000	0.004	0.002	-0.007	0.006	2.512	2.395	1.865	2.622
20 ppb	1	1	21.111	1.664	0.320	0.318	0.326	0.316	0.005	20.993	21.464	20.876	2.588
102104	1	1	71.257	0.808	1.172	1.181	1.173	1.162	0.010	71.786	71.315	70.668	2.838
102105	1	1	50.461	0.463	0.819	0.817	0.823	0.816	0.004	50.363	50.716	50.304	2.500
102106	1	1	46.851	0.661	0.757	0.762	0.758	0.752	0.005	47.126	46.890	46.537	2.573
102110	1	1	38.807	3.130	0.621	0.64	0.622	0.6	0.020	39.945	38.886	37.591	3.456
102111	1	1	36.002	4.357	0.573	0.598	0.575	0.546	0.026	37.473	36.119	34.413	3.811
Sample Blank	1	1	2.355	87.797	0.001	0.008	0.002	-0.006	0.007	2.748	2.395	1.924	2.690
102112	1	1	29.214	2.364	0.458	0.464	0.464	0.445	0.011	29.586	29.586	28.468	2.923
102204	1	1	35.825	4.013	0.570	0.586	0.581	0.543	0.024	36.767	36.473	34.236	3.661
102205	1	1	30.744	2.324	0.484	0.495	0.484	0.472	0.012	31.411	30.763	30.057	2.954
102206	1	1	29.567	7.853	0.464	0.447	0.44	0.504	0.035	28.586	28.174	31.941	4.343
102305	1	1	2.630	44.096	0.006	0.012	0.002	0.004	0.005	2.983	2.395	2.512	2.588
20 ppb	1	1	16.089	1.727	0.235	0.234	0.239	0.231	0.004	16.049	16.344	15.873	2.515

A = Automatic by instrument
Reps = Replicates
R^2 = Regression Value
M = Manual
RSD = Relative Standard Deviation
Conc = Concentration
St Dev = Standard Deviation

Sample Label	Conc ppb	%RSD	Mean Abs.	Abs. Reps			StdDev
Cal Blank	-----	1951.922	0.000	-0.006	0	0.007	0.00651
Standard 1	10	10.053	0.131	0.117	0.143	0.134	0.0132
Standard 2	25	3.356	0.260	0.253	0.27	0.258	0.00874
Standard 3	40	0.357	0.560	0.56	0.562	0.558	0.002
Standard 4	55	0.953	0.699	0.691	0.702	0.703	0.00666
Standard 5	70	1.207	0.968	0.955	0.97	0.978	0.01168

slope	70.001
intercept	3.3475
R^2 =	0.9852

Conc ppb	Mean Abs
10	0.086
25	0.171
40	0.368
55	0.459
70	0.636

Rescale Calibration

Sample Label	Conc ppb	%RSD	Mean Abs.	Abs. Reps			Std Dev
Rescale Blank	-----	20.817	-0.020	-0.021	-0.023	-0.015	0.00416
Rescale Standard	40	1.394	0.368	0.374	0.367	0.364	0.00513

slope	106.523
intercept	3.3475
R^2 =	0.9851

Sample Label	Dilution		Conc ppb	%RSD	Mean Abs	Abs Reps			Std Dev	Conc Rep			St Dev
	A	M											
Sample Blank	1	1	1.537	38.573	-0.017	-0.016	-0.011	-0.024	0.00656	1.643	2.176	0.791	3.8065
20 ppb	1	1	18.474	5.764	0.142	0.144	0.149	0.133	0.00819	18.687	19.219	17.515	3.9205
102101	1	1	40.844	2.952	0.352	0.358	0.358	0.34	0.01039	41.483	41.483	39.565	4.075
102102	1	1	36.050	6.905	0.307	0.285	0.327	0.311	0.0212	33.707	38.181	36.476	4.8313
102103	1	1	32.002	6.878	0.269	0.269	0.25	0.287	0.0185	32.002	29.978	33.920	4.6427
102301	1	1	5.158	64.795	0.017	0.03	0.01	0.012	0.01102	6.543	4.413	4.626	4.1186
102302	1	1	4.413	58.595	0.010	0.008	0.006	0.017	0.00586	4.200	3.987	5.158	3.7577
20 ppb	1	1	16.982	13.010	0.128	0.133	0.141	0.109	0.01665	17.515	18.367	14.959	4.5132

A = Automatic by instrument
Reps = Replicates
R^2 = Regression Value

M = Manual
RSD = Relative Standard Deviation

Conc = Concentration
St Dev = Standard Deviation

Sample Label	Conc ppb	%RSD	Mean Abs.	Abs. Reps			StdDev
Cal Blank	-----	24.980	0.008	0.01	0.009	0.006	0.002
Standard 1	10	6.667	0.120	0.112	0.128	0.12	0.008
Standard 2	25	3.615	0.251	0.262	0.248	0.245	0.009
Standard 3	40	0.780	0.534	0.531	0.533	0.539	0.004
Standard 4	55	1.364	0.672	0.664	0.67	0.682	0.009
Standard 5	70	1.030	0.926	0.921	0.92	0.937	0.010

slope	72.8473
intercept	3.53263
R^2 =	0.9873

Sample Label	Dilution		Conc ppb	%RSD	Mean Abs.	Abs. Reps			StdDev	Conc Rep			St Dev
	A	M											
Sample Blank	1	1	4.552	21.822	0.014	0.017	0.011	0.015	0.003	4.771	4.334	4.625	3.755
20 ppb	1	1	23.056	5.020	0.268	0.272	0.253	0.279	0.013	23.347	21.963	23.857	4.513
102107	1	1	32.162	1.147	0.393	0.398	0.393	0.389	0.005	32.526	32.162	31.870	3.861
102108	1	1	36.970	1.635	0.459	0.45	0.463	0.463	0.008	36.314	37.261	37.261	4.079
102109	1	1	32.089	0.765	0.392	0.392	0.389	0.395	0.003	32.089	31.870	32.307	3.751
102310	1	1	8.778	0.802	0.072	0.071	0.072	0.072	0.001	8.705	8.778	8.778	3.575
20 ppb	1	1	26.407	4.205	0.314	0.317	0.3	0.326	0.013	26.625	25.387	27.281	4.494

Rescale Calibration

Sample Label	Conc ppb	%RSD	Mean Abs.	Abs. Reps			St Dev
Rescale Blank	-----	1.089	0.053	0.054	0.054	0.053	0.001
Rescale Standard	40	2.006	0.549	0.538	0.55	0.56	0.011

Conc ppb	Mean Abs
10	0.135
25	0.266
40	0.549
55	0.687
70	0.941

slope	72.8473
intercept	2.43992
R^2 =	0.9873

	Dilution		Conc ppb	%RSD	Mean Abs	Abs. Reps			St Dev	Conc Rep			St Dev
	A	M											
Sample Blank	1	1	7.296	7.089	0.067	0.065	0.072	0.063	0.005	7.175	7.685	7.029	2.784
20 ppb	1	1	23.857	0.000	0.294	0.294	0.294	0.294	0.000	23.857	23.857	23.857	2.440
102312	1	1	7.394	2.547	0.068	0.066	0.069	0.069	0.002	7.248	7.466	7.466	2.566
102313	1	1	32.259	0.987	0.409	0.405	0.413	0.41	0.004	31.943	32.526	32.307	2.734
102314	1	1	32.259	1.102	0.409	0.414	0.409	0.405	0.005	32.599	32.234	31.943	2.768
102315	1	1	38.936	0.528	0.501	0.498	0.502	0.503	0.003	38.718	39.009	39.082	2.633
101417	1	1	32.914	1.679	0.418	0.419	0.411	0.425	0.007	32.963	32.380	33.400	2.952
20 ppb	1	1	22.983	6.922	0.282	0.281	0.302	0.263	0.020	22.910	24.440	21.599	3.862

A = Automatic by instrument
M = Manual
Conc = Concentration
Reps = Replicates
RSD = Relative Standard Deviation
St Dev = Standard Deviation
R^2 = Regression Value

Sample Label	Dilution		Conc ppb	%RSD	Mean Abs.	Abs Reps			St Dev	Conc Rep			St Dev
	A	M											
Sample Blank	1	1	8.243	2.899	0.080	0.077	0.081	0.081	0.002	8.049	8.341	8.341	2.608
20 ppb	1	1	23.857	0.589	0.294	0.295	0.295	0.292	0.002	23.930	23.930	23.711	2.566
102201	1	1	20.288	2.273	0.245	0.246	0.25	0.239	0.006	20.360	20.652	19.850	2.846
102202	1	1	16.184	3.449	0.189	0.182	0.189	0.195	0.007	15.698	16.208	16.645	2.914
102203	1	1	16.402	1.506	0.192	0.19	0.195	0.19	0.003	16.281	16.645	16.281	2.650
102401	1	1	5.475	6.040	0.042	0.042	0.039	0.044	0.003	5.500	5.281	5.645	2.623
102402	1	1	5.402	12.377	0.041	0.046	0.04	0.036	0.005	5.791	5.354	5.062	2.807
20 ppb	1	1	23.493	0.692	0.289	0.289	0.287	0.291	0.002	23.493	23.347	23.638	2.586
Sample Blank	1	1	7.709	2.878	0.072	0.074	0.07	0.073	0.002	7.831	7.539	7.758	2.592
20 ppb	1	1	23.906	4.077	0.295	0.283	0.307	0.294	0.012	23.056	24.804	23.857	3.315
102403	1	1	5.937	4.167	0.048	0.05	0.046	0.048	0.002	6.082	5.791	5.937	2.586
102404	1	1	4.164	24.758	0.024	0.026	0.017	0.028	0.006	4.334	3.678	4.480	2.867
102405	1	1	4.650	13.323	0.030	0.026	0.034	0.031	0.004	4.334	4.917	4.698	2.734
102406	1	1	4.965	3.331	0.035	0.036	0.034	0.034	0.001	5.062	4.917	4.917	2.524
102704	1	1	3.557	9.962	0.015	0.017	0.015	0.014	0.002	3.678	3.533	3.460	2.551
20 ppb	1	1	23.493	2.105	0.289	0.282	0.293	0.292	0.006	22.983	23.784	23.711	2.883

A = Automatic by instrument
M = Manual
Conc = Concentration
Reps = Replicates
RSD = Relative Standard Deviation
St Dev = Standard Deviation
R^2 = Regression Value

Sample Label	Conc ppb	%RSD	Mean Abs.	Abs. Reps			StDev
Cal Blank	0	101.258	0.022	0.047	0.009	0.009	0.022
Standard 1	10	6.455	0.121	0.125	0.112	0.126	0.008
Standard 2	25	2.830	0.251	0.257	0.243	0.252	0.007
Standard 3	40	0.708	0.535	0.533	0.532	0.539	0.004
Standard 4	55	0.739	0.677	0.682	0.677	0.672	0.005

slope	79.3921
intercept	0.51515
R^2 =	0.9821

Sample Label	Dilution		Conc ppb	%RSD	Mean Abs	Abs. Reps			StDev	Conc Rep			St Dev
	A	M											
Sample Blank	1	1	-0.755	38.017	-0.016	-0.009	-0.019	-0.02	0.006	-0.199	-0.993	-1.073	0.998
20 ppb	1	1	27.932	1.486	0.345	0.341	0.344	0.351	0.005	27.588	27.826	28.382	0.923
102208	1	1	13.086	4.782	0.158	0.167	0.155	0.153	0.008	13.774	12.821	12.662	1.116
102209	1	1	20.866	2.149	0.256	0.25	0.259	0.26	0.006	20.363	21.078	21.157	0.952
102504	1	1	19.516	3.403	0.239	0.23	0.245	0.243	0.008	18.775	19.966	19.807	1.162
102505	1	1	21.607	3.134	0.266	0.275	0.263	0.259	0.008	22.348	21.395	21.078	1.176
20 ppb	1	1	25.603	6.329	0.316	0.296	0.316	0.336	0.020	24.015	25.603	27.191	2.103

Rescale Calibration

Sample Label	Conc ppb	%RSD	Mean Abs	Abs. Reps			St Dev
Rescale Blank	-----	9.940	-0.034	-0.035	-0.031	-0.037	0.003
Rescale Standard	40	1.010	0.576	0.576	0.582	0.57	0.006

Conc ppb	Mean Abs
0	0.063
10	0.162
25	0.292
40	0.576
55	0.718

slope	79.3921
intercept	-2.7664
R^2 =	0.9821

Sample Label	Dilution		Conc ppb	%RSD	Mean Abs.	Abs. Reps			St Dev	Conc Rep			St Dev
	A	M											
Sample Blank	1	1	-5.307	11.267	-0.032	-0.028	-0.035	-0.033	0.004	-4.989	-5.545	-5.386	-2.480
20 ppb	1	1	24.306	2.032	0.341	0.333	0.345	0.345	0.007	23.671	24.624	24.624	-2.216
102506	1	1	23.010	0.641	0.325	0.327	0.324	0.323	0.002	23.195	22.957	22.877	-2.601
102604	1	1	18.590	1.620	0.269	0.272	0.264	0.271	0.004	18.828	18.193	18.749	-2.420
102605	1	1	28.091	1.654	0.389	0.384	0.396	0.386	0.006	27.720	28.673	27.879	-2.256
102606	1	1	28.514	0.915	0.394	0.391	0.393	0.398	0.004	28.276	28.435	28.832	-2.480
102711	1	1	2.447	6.154	0.066	0.068	0.061	0.068	0.004	2.632	2.077	2.632	-2.446
20 ppb	1	1	25.047	2.859	0.350	0.354	0.358	0.339	0.010	25.338	25.656	24.148	-1.971
Sample Blank	1	1	-5.757	6.681	-0.038	-0.035	-0.04	-0.038	0.003	-5.545	-5.942	-5.783	-2.567
20 ppb	1	1	23.618	2.953	0.332	0.321	0.338	0.338	0.010	22.718	24.068	24.068	-1.987

A = Automatic by instrument
M = Manual
Conc = Concentration
Reps = Replicates
RSD = Relative Standard Deviation
St Dev = Standard Deviation
R^2 = Regression Value

Sample Label	Conc ppb	%RSD	Mean Abs.	Abs. Reps			StDev
Cal Blank	-----	52.372	-0.012	-0.005	-0.013	-0.017	0.006
Standard 1	10	2.800	0.144	0.148	0.145	0.14	0.004
Standard 2	25	0.848	0.272	0.275	0.271	0.271	0.002
Standard 3	40	0.098	0.591	0.592	0.591	0.591	0.001
Standard 4	55	0.283	0.735	0.734	0.733	0.737	0.002
Standard 5	70	0.684	0.995	0.987	0.997	1	0.007

slope	68.2807
intercept	2.61859
R^2 =	0.9847

Sample Label	Dilution		Conc ppb	%RSD	Mean Abs	Abs. Reps			StDev	Conc Rep			St Dev
	A	M											
Sample Blank	1	1		94.187	-0.013	0.001	-0.021	-0.018	0.012	2.687	1.185	1.390	3.433
20 ppb	1	1	23.421	0.758	0.305	0.302	0.306	0.306	0.002	23.239	23.512	23.512	2.776

Rescale Calibration

Sample Label	Conc ppb	%RSD	Mean Abs.	Abs. Reps			St Dev
Rescale Blank	-----	28.868	-0.014	-0.011	-0.018	-0.011	0.004
Rescale Standard	40	1.426	0.599	0.591	0.598	0.608	0.009

Conc ppb	Mean Abs
0	-0.004
10	0.152
25	0.280
40	0.599
55	0.742
70	1.002

slope	69.4346
intercept	1.25839
R^2 =	0.9847

Sample Label	Dilution		Conc ppb	%RSD	Mean Abs.	Abs. Reps			St Dev	Conc Rep			St Dev
	A	M											
Sample Blank	1	1	0.309	29.572	-0.014	-0.009	-0.016	-0.016	0.004	2.004	1.526	1.526	1.539
20 ppb	1	1	23.639	0.997	0.322	0.32	0.326	0.321	0.003	24.468	24.878	24.537	1.482
102707	1	1	22.251	0.832	0.302	0.305	0.3	0.302	0.003	23.444	23.103	23.239	1.433
102708	1	1	36.300	0.750	0.505	0.502	0.503	0.509	0.004	36.896	36.964	37.373	1.521
102709	1	1	46.298	0.541	0.649	0.652	0.649	0.645	0.004	47.138	46.933	46.660	1.502
102710	1	1	38.174	0.217	0.532	0.533	0.531	0.531	0.001	39.012	38.876	38.876	1.339
102712	1	1	23.269	0.315	0.317	0.317	0.318	0.316	0.001	24.264	24.332	24.195	1.328
20 ppb	1	1	24.820	1.776	0.339	0.34	0.333	0.345	0.006	25.834	25.356	26.175	1.677

A = Automatic by instrument
Reps = Replicates
R^2 = Regression Value

M = Manual
RSD = Relative Standard Deviation

Conc = Concentration
St Dev = Standard Deviation

Rescale Calibration

Sample Label	Conc ppb	%RSD	Mean Abs.	Abs. Reps			St Dev
Rescale Blank	-----	37.500	-0.008	-0.005	-0.011	-0.008	0.003
Rescale Standard	40	1.229	0.616	0.611	0.613	0.625	0.008

Conc ppb	Mean Abs
0	0.013
10	0.169
25	0.297
40	0.616
55	0.759
70	1.019

slope	69.4346
intercept	0.078
R^2 =	0.9899

Sample Label	Dilution		Conc ppb	%RSD	Mean Abs.	Abs. Reps			St Dev	Conc Rep			St Dev
	A	M											
Sample Blank	1	1	-0.709	39.787	-0.011	-0.007	-0.011	-0.016	0.005	-0.408	-0.686	-1.033	0.391
20 ppb	1	1	23.547	2.712	0.338	0.34	0.346	0.328	0.009	23.686	24.102	22.853	0.714
102501	0.5	1	84.496	1.657	0.607	0.618	0.606	0.598	0.010	85.977	84.311	83.200	1.554
102502	1	1	21.927	3.724	0.315	0.328	0.306	0.31	0.012	22.853	21.325	21.603	0.892
102503	1	1	23.732	2.124	0.341	0.349	0.337	0.336	0.007	24.311	23.477	23.408	0.580
102601	1	1	19.659	1.418	0.282	0.286	0.282	0.278	0.004	19.936	19.659	19.381	0.356
102602	0.2	1	205.222	0.777	0.590	0.589	0.595	0.586	0.005	204.875	206.958	203.833	1.981
20 ppb	1	1	17.923	2.059	0.257	0.251	0.261	0.259	0.005	17.506	18.200	18.062	0.445

A = Automatic by instrument
M = Manual
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RSD = Relative Standard Deviation
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R^2 = Regression Value

Rescale Calibration

Sample Label	Conc ppb	%RSD	Mean Abs.	Abs. Reps			St Dev
Rescale Blank	-----	10.000	-0.020	-0.007	-0.009	-0.011	0.002
Rescale Standard	40	11.729	0.473	0.486	0.428	0.539	0.056

Conc ppb	Mean Abs
0	0.013
10	0.169
25	0.297
40	0.473
55	0.617
70	0.877

slope	84.8221
intercept	-1.2364
R^2 =	0.9896

Sample Label	Dilution		Conc ppb	%RSD	Mean Abs.	Abs. Reps			St Dev	Conc Rep			St Dev
	A	M											
Sample Blank	1	1	-2.085	52.915	-0.010	-0.016	-0.006	-0.008	0.005	-2.594	-1.745	-1.915	-0.788
20 ppb	1	1	17.933	9.036	0.226	0.249	0.21	0.219	0.020	19.884	16.576	17.340	0.496
102603	1	1	13.890	3.978	0.178	0.186	0.172	0.177	0.007	14.541	13.353	13.777	-0.635
102713	1	1	19.206	1.496	0.241	0.242	0.237	0.244	0.004	19.291	18.866	19.460	-0.931
102701	1	1	37.103	0.442	0.452	0.454	0.452	0.45	0.002	37.273	37.103	36.934	-1.067
102702	1	1	93.482	0.897	1.117	1.107	1.127	1.116	0.010	92.662	94.358	93.425	-0.387
102702	0.5	1	96.599	1.975	0.584	0.595	0.585	0.572	0.012	98.466	96.769	94.564	-0.516
102703	0.2	1	175.903	4.798	0.429	0.427	0.451	0.41	0.021	174.913	185.092	167.703	2.554
20 ppb	1	1	16.746	7.591	0.212	0.23	0.199	0.207	0.016	18.273	15.643	16.322	0.129

Sample Label	Conc ppb	%RSD	Mean Abs.	Abs. Reps			Std Dev
Cal Blank	-----	28.571	0.007	0.007	0.009	0.005	0.002
Standard 1	10	4.764	0.160	0.152	0.162	0.167	0.008
Standard 2	25	1.568	0.315	0.309	0.317	0.318	0.005
Standard 3	40	0.675	0.646	0.651	0.643	0.644	0.004
Standard 4	55	2.677	0.809	0.796	0.797	0.834	0.022
Standard 5	70	1.248	1.084	1.071	1.083	1.098	0.014

slope	63.3184
intercept	1.83164
R^ =	0.9885

Sample Label	Dilution		Conc ppb	%RSD	Mean Abs.	Abs. Reps			Std Dev	Conc Rep			St Dev
	A	M											
Sample Blank	1	1	2.556	40.984	0.016	0.023	0.015	0.01	0.007	3.288	2.781	2.465	1.946
20 ppb	1	1	20.040	2.905	0.287	0.284	0.28	0.296	0.008	19.814	19.561	20.574	2.060
102802	1	1	35.349	1.271	0.524	0.531	0.522	0.518	0.007	35.454	34.884	34.631	1.953
102803	1	1	45.211	1.231	0.676	0.667	0.683	0.679	0.008	44.065	45.078	44.825	2.060
102804	1	1	19.674	1.068	0.281	0.278	0.281	0.284	0.003	19.434	19.624	19.814	1.716
20 ppb	1	1	20.126	8.420	0.288	0.302	0.302	0.26	0.024	20.954	20.954	18.294	3.089

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Sample Label	Conc ppb	%RSD	Mean Abs.	Abs. Reps			Std Dev
Cal Blank	-----	57.735	0.009	0.012	0.012	0.003	0.005
Standard 1	10	3.538	0.156	0.15	0.156	0.161	0.006
Standard 2	25	1.494	0.316	0.318	0.311	0.32	0.005
Standard 3	40	1.395	0.647	0.638	0.646	0.656	0.009
Standard 4	55	0.547	0.797	0.802	0.794	0.795	0.004
Standard 5	70	1.278	1.063	1.07	1.047	1.071	0.014

slope	64.5958
intercept	1.52245
R^ =	0.988

Sample Label	Dilution		Conc ppb	%RSD	Mean Abs.	Abs. Reps			Std Dev	Conc Rep			St Dev
	A	M											
Sample Blank	1	1	2.685	24.216	0.018	0.023	0.015	0.016	0.004	3.008	2.491	2.556	1.804
20 ppb	1	1	21.073	2.691	0.303	0.297	0.312	0.299	0.008	20.707	21.676	20.837	2.049
102805	1	1	17.994	2.075	0.255	0.259	0.249	0.257	0.005	18.253	17.607	18.124	1.864
102806	1	1	15.690	1.466	0.219	0.218	0.223	0.217	0.003	15.604	15.927	15.540	1.730
102901	1	1	26.112	1.062	0.381	0.383	0.376	0.383	0.004	26.263	25.810	26.263	1.784
102902	1	1	40.926	1.712	0.610	0.622	0.605	0.603	0.010	41.701	40.603	40.474	2.197
102903	1	1	38.622	1.812	0.574	0.586	0.571	0.566	0.010	39.376	38.407	38.084	2.195
20 ppb	1	1	21.827	2.743	0.314	0.322	0.305	0.316	0.009	22.322	21.224	21.935	2.079
Sample Blank	1	1	2.857	7.391	0.021	0.021	0.022	0.019	0.002	2.879	2.944	2.750	1.621
20 ppb	1	1	22.990	0.695	0.332	0.331	0.331	0.335	0.002	22.904	22.904	23.162	1.672
102714	1	1	24.583	0.560	0.357	0.359	0.357	0.355	0.002	24.712	24.583	24.454	1.652
102801	1	1	31.559		0.465	0.465				31.559			
102607	1	1	33.368	3.800	0.493	0.472	0.499	0.508	0.019	32.012	33.756	34.337	2.733
102608	1	1	22.602	3.219	0.326	0.316	0.326	0.337	0.011	21.935	22.581	23.291	2.201
102609	1	1	21.547	3.414	0.310	0.302	0.322	0.306	0.011	21.030	22.322	21.289	2.206
102705	1	1	61.467	0.855	0.928	0.919	0.934	0.931	0.008	60.886	61.855	61.661	2.035
102706	1	1	61.274	1.689	0.925	0.915	0.917	0.943	0.016	60.628	60.757	62.436	2.531
Sample Blank	1	1	2.599	24.249	0.017	0.016	0.013	0.021	0.004	2.556	2.362	2.879	1.784
20 ppb	1	1	22.042	1.419	0.318	0.313	0.322	0.318	0.005	21.741	22.322	22.064	1.814

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Sample Label	Conc ppb	%RSD	Mean Abs.	Abs. Reps			StdDev
Cal Blank	-----	22.048	0.012	0.01	0.015	0.011	0.003
Standard 1	10	0.000	0.186	0.186	0.186	0.186	0.000
Standard 2	25	0.993	0.363	0.367	0.362	0.36	0.004
Standard 3	40	0.899	0.695	0.69	0.693	0.702	0.006
Standard 4	55	0.582	0.865	0.866	0.87	0.86	0.005
Standard 5	70	0.780	1.156	1.147	1.157	1.165	0.009

slope	60.8334
intercept	0.26767
R^2 =	0.9907

Sample Label	Dilution		Conc ppb	%RSD	Mean Abs.	Abs. Reps			StdDev	Conc Rep			St Dev
	A	M											
Sample Blank	1	1	1.768	4.681	0.025	0.024	0.026	0.024	0.001	1.728	1.849	1.728	0.338
Check Sample	1	1	20.809	1.461	0.338	0.341	0.34	0.332	0.005	21.012	20.951	20.464	0.568
Sample Blank	1	1	1.241	28.641	0.016	0.015	0.012	0.021	0.005	1.180	0.998	1.545	0.546
Sample Blank	1	1	1.079	38.487	0.013	0.009	0.019	0.012	0.005	0.815	1.424	0.998	0.580
112310	0.5	0.25	384.500	1.475	0.786	0.798	0.784	0.775	0.012	390.502	383.689	379.309	7.782
Sample Blank	1	1	1.829	12.524	0.026	0.027	0.022	0.028	0.003	1.910	1.606	1.971	0.463
112311	0.5	0.25	350.433	0.807	0.716	0.719	0.719	0.709	0.006	352.055	352.055	347.188	4.951
Periodic Check	1	1	21.377	0.576	0.347	0.347	0.345	0.349	0.002	21.377	21.255	21.499	0.389
Sample Blank	1	1	1.484	13.229	0.020	0.018	0.019	0.023	0.003	1.363	1.424	1.667	0.429
112312	0.5	0.25	346.540	1.498	0.708	0.719	0.706	0.698	0.011	352.055	345.728	341.835	7.299
Sample Blank	1	1	2.012	13.207	0.029	0.033	0.026	0.027	0.004	2.275	1.849	1.910	0.498
112407	0.2	0.5	350.035	1.226	0.571	0.574	0.563	0.576	0.007	351.860	345.169	353.077	6.935
Sample Blank	1	1	2.579	16.007	0.038	0.045	0.035	0.034	0.006	3.005	2.397	2.336	0.638
112408	0.2	0.5	351.455	2.303	0.573	0.585	0.576	0.559	0.013	358.552	353.077	342.735	10.709
Sample Blank	1	1	2.640	19.359	0.039	0.046	0.031	0.04	0.008	3.066	2.154	2.701	0.727
112409	0.2	0.5	363.013	1.569	0.592	0.595	0.6	0.582	0.009	364.636	367.677	356.727	8.329
Periodic Check	1	1	21.620	0.570	0.351	0.353	0.349	0.351	0.002	21.742	21.499	21.620	0.389
Sample Blank	1	1	2.640	6.784	0.039	0.041	0.036	0.04	0.003	2.762	2.458	2.701	0.429
112501	0.5	0.25	357.084	1.589	0.729	0.717	0.731	0.74	0.012	351.082	357.895	362.275	7.782
Sample Blank	1	1	2.965	11.127	0.044	0.05	0.041	0.042	0.005	3.309	2.762	2.823	0.568
112502	0.5	0.25	370.711	1.323	0.757	0.747	0.767	0.758	0.010	365.682	375.415	371.035	7.016
Sample Blank	1	1	2.802	22.300	0.042	0.052	0.034	0.039	0.009	3.431	2.336	2.640	0.833
112503	0.5	0.25	366.980	0.858	0.750	0.757	0.747	0.745	0.006	370.549	365.682	364.709	5.270
Sample Blank	1	1	2.762	19.512	0.041	0.049	0.041	0.033	0.008	3.249	2.762	2.275	0.754
112504	0.5	0.25	360.653	1.451	0.737	0.746	0.739	0.725	0.011	365.195	361.788	354.975	7.345
Periodic Check	1	1	21.904	0.859	0.356	0.353	0.359	0.355	0.003	21.742	22.107	21.864	0.454
Sample Blank	1	1	2.417	16.093	0.035	0.04	0.037	0.029	0.006	2.701	2.519	2.032	0.614
112505	0.5	0.25	367.466	2.721	0.751	0.742	0.736	0.774	0.020	363.248	360.328	378.822	12.083
Sample Blank	1	1	2.539	20.104	0.037	0.046	0.033	0.033	0.008	3.066	2.275	2.275	0.724
112506	0.5	0.25	373.306	2.379	0.763	0.782	0.76	0.746	0.018	382.715	372.009	365.195	10.973
Sample Blank	1	1	2.539	15.465	0.037	0.044	0.034	0.034	0.006	2.944	2.336	2.336	0.619
112313	1	0.5	88.217	0.561	0.721	0.716	0.723	0.723	0.004	87.649	88.500	88.500	1.027
Sample Blank	1	1	2.579	19.868	0.038	0.039	0.045	0.03	0.008	2.640	3.005	2.093	0.727
112314	1	0.5	88.744	1.379	0.725	0.715	0.725	0.735	0.010	87.527	88.744	89.960	1.752

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Sample Label	Dilution		Conc ppb	%RSD	Mean Abs.	Abs. Reps			StdDev	Conc Rep			StdDev
	A	M											
Periodic Check	1	1	21.275	1.017	0.345	0.345	0.349	0.342	0.004	21.255	21.499	21.073	0.481
Sample Blank	1	1	1.951	9.096	0.028	0.03	0.028	0.025	0.003	2.093	1.971	1.789	0.421
112315	1	0.5	93.124	0.131	0.761	0.76	0.762	0.761	0.001	93.002	93.245	93.124	0.657
Sample Blank	1	1	2.072	22.444	0.030	0.037	0.024	0.028	0.007	2.519	1.728	1.971	0.673
112410	1	0.5	87.122	1.036	0.712	0.706	0.72	0.709	0.007	86.432	88.135	86.797	1.432
Sample Blank	1	1	2.113	23.389	0.030	0.038	0.024	0.029	0.007	2.579	1.728	2.032	0.699
112411	1	0.5	84.364	0.768	0.689	0.685	0.695	0.687	0.005	83.877	85.094	84.120	1.179
Sample Blank	1	1	2.052	21.917	0.029	0.032	0.034	0.022	0.006	2.214	2.336	1.606	0.659
112412	1	0.5	88.987	1.175	0.727	0.718	0.728	0.735	0.009	87.892	89.109	89.960	1.575
Periodic Check	1	1	22.208	2.241	0.361	0.37	0.356	0.356	0.008	22.776	21.924	21.924	0.759
Sample Blank	1	1	1.890	15.155	0.027	0.031	0.023	0.026	0.004	2.154	1.667	1.849	0.514
112507	1	0.5	88.663	0.523	0.724	0.727	0.726	0.72	0.004	88.987	88.865	88.135	0.996
Sample Blank	1	1	1.910	16.144	0.027	0.032	0.024	0.025	0.004	2.214	1.728	1.789	0.533
112508	1	0.5	75.725	0.856	0.618	0.616	0.614	0.624	0.005	75.482	75.239	76.455	1.179
Sample Blank	1	1	1.971	25.000	0.028	0.035	0.028	0.021	0.007	2.397	1.971	1.545	0.694
112509	1	0.5	85.621	0.676	0.699	0.694	0.703	0.701	0.005	84.972	86.067	85.824	1.110
Sample Blank	1	1	2.681	39.887	0.040	0.057	0.036	0.026	0.016	3.735	2.458	1.849	1.230
112510	1	0.5	84.445	0.084	0.690	0.69	0.689	0.69	0.001	84.485	84.364	84.485	0.606
Periodic Check	1	1	20.302	2.582	0.329	0.339	0.323	0.326	0.009	20.890	19.917	20.099	0.785
Sample Blank	1	1	1.890	24.969	0.027	0.034	0.025	0.021	0.007	2.336	1.789	1.545	0.673
112511	1	0.5	79.740	0.922	0.651	0.657	0.645	0.651	0.006	80.470	79.010	79.740	1.265
Sample Blank	1	1	2.174	35.155	0.031	0.044	0.026	0.024	0.011	2.944	1.849	1.728	0.938
112512	1	0.5	78.240	0.706	0.639	0.643	0.634	0.639	0.005	78.767	77.672	78.280	1.084
Check Sample	1	1	19.876	0.474	0.322	0.322	0.324	0.321	0.002	19.856	19.978	19.795	0.361

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Sample Label	Conc ppb	% RSD	Mean Abs.	Abs. Reps			StdDev
Cal Blank	-----	121.848	-0.005	-0.003	0	-0.011	0.006
Standard 1	10	6.783	0.195	0.209	0.183	0.192	0.013
Standard 2	25	1.584	0.334	0.332	0.34	0.33	0.005
Standard 3	40	0.897	0.634	0.632	0.629	0.64	0.006
Standard 4	55	0.580	0.790	0.795	0.789	0.786	0.005
Standard 5	70	0.054	1.074	1.074	1.073	1.074	0.001

slope	66.8869
intercept	-0.48
R^2 =	0.9872

Sample Label	Dilution		Conc ppb	% RSD	Mean Abs.	Abs. Reps			StdDev	Conc Rep			St Dev
	A	M											
Sample Blank	1	1	-2.041	25.833	-0.023	-0.017	-0.024	-0.029	0.006	-1.617	-2.085	-2.420	-0.077
Check Sample	1	1	21.214	1.982	0.324	0.317	0.327	0.329	0.006	20.723	21.392	21.526	-0.050
111804	1	1	7.301	3.970	0.116	0.119	0.119	0.111	0.005	7.480	7.480	6.944	-0.171
Sample Blank	1	1	-0.547	435.890	-0.001	0.004	-0.004	-0.003	0.004	-0.212	-0.748	-0.681	-0.188
111805	1	1	8.639	2.964	0.136	0.137	0.132	0.14	0.004	8.684	8.349	8.884	-0.210
Sample Blank	1	1	-0.458	916.515	0.000	0.001	0.003	-0.003	0.003	-0.413	-0.279	-0.681	-0.276
111806	1	1	7.747	2.816	0.123	0.127	0.121	0.121	0.003	8.015	7.613	7.613	-0.248
Sample Blank	1	1	-0.814	34.641	-0.005	-0.003	-0.006	-0.006	0.002	-0.681	-0.881	-0.881	-0.364
111901	1	1	7.948	15.142	0.126	0.114	0.116	0.148	0.019	7.145	7.279	9.419	0.796
Periodic Check	1	1	21.414	2.822	0.327	0.322	0.338	0.322	0.009	21.058	22.128	21.058	0.138
Sample Blank	1	1	-1.127	58.823	-0.010	-0.005	-0.008	-0.016	0.006	-0.814	-1.015	-1.550	-0.100
111902	1	1	8.572	1.860	0.135	0.138	0.135	0.133	0.003	8.750	8.550	8.416	-0.312
Sample Blank	1	1	-1.216	56.773	-0.011	-0.004	-0.016	-0.013	0.006	-0.748	-1.550	-1.350	-0.062
111903	1	1	10.267	2.001	0.161	0.163	0.162	0.157	0.003	10.423	10.356	10.021	-0.265
Sample Blank	1	1	-0.814	131.149	-0.005	-0.012	0.001	-0.004	0.007	-1.283	-0.413	-0.748	-0.041
112001	1	1	8.438	1.561	0.133	0.135	0.134	0.131	0.002	8.550	8.483	8.282	-0.341
Sample Blank	1	1	-1.216	39.626	-0.011	-0.006	-0.014	-0.013	0.004	-0.881	-1.416	-1.350	-0.188
112002	1	1	10.601	1.844	0.166	0.165	0.169	0.163	0.003	10.556	10.824	10.423	-0.276
Periodic Check	1	1	22.150	1.195	0.338	0.339	0.334	0.342	0.004	22.195	21.860	22.395	-0.210
Sample Blank	1	1	-1.104	43.301	-0.009	-0.01	-0.005	-0.013	0.004	-1.149	-0.814	-1.350	-0.210
112003	1	1	11.738	4.145	0.183	0.174	0.188	0.186	0.008	11.158	12.095	11.961	0.026
Sample Blank	1	1	-0.970	34.317	-0.007	-0.01	-0.005	-0.007	0.003	-1.149	-0.814	-0.948	-0.312
112004	1	1	8.728	2.936	0.138	0.133	0.14	0.14	0.004	8.416	8.884	8.884	-0.210
Sample Blank	1	1	-1.037	107.555	-0.008	0.002	-0.014	-0.013	0.009	-0.346	-1.416	-1.350	0.120
112005	1	1	13.767	2.484	0.213	0.215	0.207	0.217	0.005	13.901	13.366	14.034	-0.126
Sample Blank	1	1	-1.015	33.072	-0.008	-0.005	-0.01	-0.009	0.003	-0.814	-1.149	-1.082	-0.303
112006	1	1	9.152	4.224	0.144	0.147	0.148	0.137	0.006	9.352	9.419	8.684	-0.073
Periodic Check	1	1	18.605	1.231	0.285	0.289	0.282	0.285	0.004	18.850	18.382	18.583	-0.245

A = Automatic by instrument
Reps = Replicates
R^2 = Regression Value

M = Manual
RSD = Relative Standard Deviation

Conc = Concentration
St Dev = Standard Deviation

Sample Label	Dilution		Conc ppb	% RSD	Mean Abs.	Abs. Reps			StdDev	Conc Rep			St Dev
	A	M											
Sample Blank	1	1	-0.904	48.238	-0.006	-0.007	-0.003	-0.009	0.003	-0.948	-0.681	-1.082	-0.276
112207	1	1	-0.502	1652.271	0.000	0	-0.006	0.005	0.006	-0.480	-0.881	-0.146	-0.112
Sample Blank	1	1	-1.238	33.405	-0.011	-0.014	-0.013	-0.007	0.004	-1.416	-1.350	-0.948	-0.227
112204	1	1	13.968	1.389	0.216	0.216	0.213	0.219	0.003	13.968	13.767	14.168	-0.279
Sample Blank	1	1	-1.171	61.460	-0.010	-0.003	-0.014	-0.014	0.006	-0.681	-1.416	-1.416	-0.055
112205	1	1	12.719	48.153	0.197	0.26	0.244	0.088	0.095	16.911	15.840	5.406	5.876
Sample Blank	1	1	-0.792	125.560	-0.005	-0.009	0.002	-0.007	0.006	-1.082	-0.346	-0.948	-0.088
112206	1	1	4.358	8.888	0.072	0.075	0.065	0.077	0.006	4.537	3.868	4.670	-0.050
Periodic Check	1	1	5.139	50.606	0.084	0.133	0.062	0.057	0.043	8.416	3.667	3.333	2.363

A = Automatic by instrument
M = Manual
Conc = Concentration
Reps = Replicates
RSD = Relative Standard Deviation
St Dev = Standard Deviation
R^2 = Regression Value

Sample Label	Conc ppb	%RSD	Mean Abs.	Abs. Reps			StdDev
Cal Blank	-----	46.188	0.013	0.01	0.01	0.018	0.005
Standard 1	10	1.360	0.183	0.185	0.18	0.183	0.003
Standard 2	25	0.709	0.355	0.355	0.352	0.357	0.003
Standard 3	40	0.435	0.689	0.689	0.692	0.686	0.003
Standard 4	55	1.069	0.859	0.849	0.86	0.867	0.009
Standard 5	70	0.391	1.171	1.172	1.175	1.166	0.005

slope	59.812
intercept	1.051
R^2 =	0.989

Sample Label	Dilution		Conc ppb	%RSD	Mean Abs.	Abs. Reps			StdDev	Conc Rep			StdDev
	A	M											
Sample Blank	1	1	1.908	18.042	0.014	0.016	0.011	0.016	0.003	2.008	1.709	2.008	1.223
Check Sample	1	1	23.121	2.786	0.369	0.359	0.379	0.369	0.010	22.523	23.719	23.121	1.649
112207	1	1	2.008	18.750	0.016	0.016	0.013	0.019	0.003	2.008	1.828	2.187	1.230
112204	1	1	17.718	2.456	0.279	0.286	0.272	0.278	0.007	18.157	17.319	17.678	1.471
112205	1	1	21.247	1.127	0.338	0.336	0.342	0.335	0.004	21.147	21.506	21.088	1.277
112206	1	1	22.144	1.079	0.353	0.351	0.357	0.35	0.004	22.045	22.403	21.985	1.277
Periodic Check	1	1	23.799	0.546	0.380	0.381	0.382	0.378	0.002	23.839	23.899	23.659	1.175
112301	1	1	18.556	1.384	0.293	0.292	0.297	0.289	0.004	18.516	18.815	18.336	1.292
112302	1	1	20.589	1.831	0.327	0.32	0.331	0.329	0.006	20.190	20.848	20.729	1.401
112303	1	1	22.683	1.129	0.362	0.358	0.366	0.361	0.004	22.463	22.942	22.643	1.292
112401	1	1	16.163	1.848	0.253	0.25	0.25	0.258	0.005	16.004	16.004	16.482	1.327
Sample Blank	1	1	1.429	138.778	0.006	0.003	0.005	0.011	0.004	1.230	1.350	1.709	1.300
112402	1	1	17.280	3.234	0.271	0.263	0.28	0.271	0.009	16.781	17.798	17.260	1.559
Periodic Check	1	1	23.201	0.823	0.370	0.371	0.367	0.373	0.003	23.241	23.002	23.360	1.233

A = Automatic by instrument
M = Manual
Conc = Concentration
Reps = Replicates
RSD = Relative Standard Deviation
St Dev = Standard Deviation
R^2 = Regression Value

Sample Label	Dilution		Conc Abs	%RSD	Mean Abs	Abs Reps			St Dev	Conc Reps			St Dev
	A	M											
Periodic Check	1	1	23.201	0.823	0.370	0.371	0.367	0.373	0.003	23.241	23.002	23.360	1.233
112403	1	1	20.788	0.303	0.330	0.33	0.331	0.329	0.001	20.788	20.848	20.729	1.110
112404	1	1	16.223	2.474	0.254	0.247	0.259	0.255	0.006	15.824	16.542	16.303	1.416
Sample Blank	1	1	1.210	-404.145	0.003	-0.001	0.007	0.002	0.004	0.991	1.469	1.170	1.292
112405	1	1	17.359	0.421	0.273	0.274	0.272	0.272	0.001	17.439	17.319	17.319	1.120
112406	1	1	20.848	1.086	0.331	0.332	0.334	0.327	0.004	20.908	21.028	20.609	1.266
Periodic Check	1	1	22.643	2.188	0.361	0.357	0.37	0.356	0.008	22.403	23.181	22.344	1.518
112208	1	1	1.589	44.096	0.009	0.006	0.01	0.011	0.003	1.409	1.649	1.709	1.209
Sample Blank	1	1	1.230	86.603	0.003	0.002	0.005	0.002	0.002	1.170	1.350	1.170	1.154
102210	1	0.1	738.215	2.250	1.217	1.229	1.236	1.185	0.028	745.592	749.779	719.275	27.042
102210	0.5	0.1	673.757	3.748	0.546	0.57	0.537	0.53	0.021	702.866	663.390	655.016	46.566
102307	1	1	39.988	1.319	0.651	0.661	0.647	0.645	0.009	40.586	39.749	39.629	1.572
Periodic Check	1	1	17.319	2.295	0.272	0.265	0.275	0.276	0.006	16.901	17.499	17.559	1.414
Sample Blank	1	1	0.991	-83.333	-0.001	-0.006	0.004	-0.001	0.005	0.692	1.290	0.991	1.350
102308	1	1	38.293	2.224	0.623	0.638	0.62	0.61	0.014	39.210	38.134	37.536	1.899
102309	1	1	33.708	0.659	0.546	0.547	0.549	0.542	0.004	33.768	33.887	33.469	1.266
102207	1	1	20.529	3.360	0.326	0.321	0.338	0.318	0.011	20.250	21.267	20.071	1.696
Sample Blank	1	1	0.911	157.527	-0.002	0.003	-0.004	-0.006	0.005	1.230	0.811	0.692	1.333
102211	1	1	8.049	3.540	0.117	0.113	0.117	0.121	0.004	7.809	8.049	8.288	1.290
Periodic Check	1	1	20.968	5.243	0.333	0.314	0.342	0.343	0.016	19.831	21.506	21.566	2.035
102212	1	1	6.872	4.071	0.097	0.093	0.099	0.1	0.004	6.613	6.972	7.032	1.277
102213	1	1	6.793	2.083	0.096	0.096	0.094	0.098	0.002	6.793	6.673	6.912	1.170
Sample Blank	1	1	1.210	208.167	0.003	0.001	0.005	0.002	0.002	1.110	1.350	1.170	1.175
102214	1	1	24.636	1.927	0.394	0.403	0.392	0.388	0.008	25.155	24.497	24.258	1.515
102215	1	1	26.590	1.620	0.427	0.432	0.43	0.419	0.007	26.889	26.770	26.112	1.469
Periodic Check	1	1	17.838	1.824	0.281	0.276	0.286	0.28	0.005	17.559	18.157	17.798	1.352
102216	1	1	20.968	1.929	0.333	0.34	0.332	0.327	0.007	21.387	20.908	20.609	1.443
Sample Blank	1	1	0.971	208.167	-0.001	0.001	-0.003	-0.002	0.002	1.110	0.871	0.931	1.175
102217	1	1	2.506	14.612	0.024	0.022	0.028	0.023	0.003	2.366	2.725	2.426	1.243
102218	1	1	4.759	6.943	0.062	0.066	0.063	0.057	0.005	4.998	4.819	4.460	1.325
102219	1	1	4.340	1.852	0.055	0.054	0.056	0.055	0.001	4.280	4.400	4.340	1.110
Periodic Check	1	1	15.146	4.906	0.236	0.238	0.246	0.223	0.012	15.286	15.764	14.389	1.749
Periodic Check	1	1	13.910	9.547	0.215	0.194	0.229	0.222	0.019	12.654	14.747	14.329	2.158
Sample Blank	1	1	1.051	90.139	0.000	0.004	-0.001	-0.003	0.004	1.290	0.991	0.871	1.266
102303	1	1	2.147	3.208	0.018	0.018	0.019	0.018	0.001	2.127	2.187	2.127	1.085
102306	1	1	1.170	87.178	0.002	0.005	0.004	-0.003	0.004	1.350	1.290	0.871	1.311

A = Automatic by instrument
Reps = Replicates
M = Manual
RSD = Relative Standard Deviation
R^2 = Regression Value
Conc = Concentration
St Dev = Standard Deviation

slope	101.294
intrcpt	-14.507
R^2 =	0.988

Sample Label	Conc ppm	%RSD	Mean Abs.	Abs. Reps										Std Dev
Cal Blank	0	42.164	-0.002	-0.002	-0.001	-0.003	-0.004	-0.002	-0.002	-0.002	-0.003	-0.003	-0.002	0.001
Standard 2	10	0.874	0.236	0.240	0.236	0.236	0.236	0.233	0.235	0.237	0.239	0.234	0.236	0.002
Standard 3	25	1.339	0.400	0.398	0.401	0.404	0.404	0.402	0.394	0.399	0.405	0.403	0.388	0.005
Standard 4	50	1.107	0.633	0.627	0.636	0.622	0.629	0.634	0.627	0.636	0.631	0.644	0.642	0.007

Sample Blank	-14.507	68.493	0.000	0.003	0.003	0.002	0.000	-0.001	-0.001	0.000	-0.002	-0.001	-0.003	0.002

Sample Label	Dilution		Conc ppm	%RSD	Mean Abs.	Abs. Reps									Std Dev
	A	M													
121501	1	0.5	103.903	3.295	0.656	0.615	0.673	0.677	0.668	0.676	0.663	0.657	0.649	0.652	0.631	0.020
121502	1	0.5	65.776	4.053	0.468	0.467	0.485	0.487	0.475	0.429	0.445	0.457	0.475	0.475	0.484	0.019
121503	1	0.5	72.766	1.413	0.502	0.504	0.486	0.511	0.497	0.500	0.504	0.504	0.502	0.506	0.510	0.007

Conc Reps										Conc St Dev
95.577	107.327	108.138	106.314	107.935	105.301	104.086	102.46	103.073	98.819	-24.910
65.594	69.241	69.646	67.215	57.896	61.137	63.568	67.21	67.215	69.038	-25.180
73.090	69.443	74.508	71.672	72.279	73.090	73.090	72.68	73.495	74.305	-27.572

A = Automatic by instrument
Reps = Replicates

M = Manual
RSD = Relative Standard Deviation
R^2 = Regression Value

Conc = Concentration
St Dev = Standard Deviation

APPENDIX B: Statistical Procedures for the Dunnett's Test

The statistical analysis performed on the chromium concentrations of the paint samples was the two-tailed Dunnett's test. This is a powerful test for the alternative hypothesis. It assumes the distribution of each mean value is normal. It compares the mean of sets of experimental data individually with the mean of a control rather than all pairwise comparisons. This assures that the familywise Type 1 error rate (œ) will not exceed 0.05 (Sheskin, 362: 1997). In this thesis, the filtered samples are the experimental data and the control is the unfiltered sample. The hypotheses are as follows:

H_o = Strontium chromate dissociation is not influenced when bound in paint

H_a = Strontium chromate dissociation is influenced when bound in paint

$$H_o: \mu_{control} = \mu_{experiment}$$

$$H_a: \mu_{control} \neq \mu_{experiment}$$

The test values required (the test statistic, critical distance calculations, and harmonic mean (n)) are listed below:

$$\text{test statistic}(t_D) := \frac{\overline{X}_a - \overline{X}_b}{\sqrt{\frac{2MS_{WG}}{n}}} \qquad (1)$$

$$\text{critical distance}(CD_D) = t_{D(k,df_{WG})} * \sqrt{\frac{2MS_{WG}}{n}} \qquad (2)$$

$$n = \frac{k}{\left(\frac{1}{n_1} + \frac{1}{n_2} + \ldots + \frac{1}{n_k}\right)} \qquad (3)$$

Where:

X_a =	Experiment Mean
X_b =	Control Mean
MS_{WG} =	Mean Squared Error
WG =	Within group
n =	Harmonic mean (mean of sample size)
k =	Number of treatments
df_{WG} =	Degrees of freedom within goup
$t_{D(k,dfWG)}$ =	Tabled critical value for Dunnett's modified t statistic

There are two ways to perform a Dunnett's test. The test statistic (t_D) is calculated for each experimental data point. The critical t value (t_{crit}) is found in a Dunnett's table using experiment values. If $t_D \geq t_{crit}$ then the difference is significant.

Alternatively, the critical distance is calculated ($t_{crit} = t_{D(k,\ dfwg)}$.). The critical distance is the minimum difference required for data to be significantly different. The control mean subtracted from the experiment mean is compared to the critical difference.

$$\overline{X}_a - \overline{X}_b \geq CD_d \qquad (4)$$

If the above equation is true, the two data are significantly different. JMP Statistics is the computer tool used to calculate these test statistics, critical values and critical differences.

Appendix C: Statistical Results

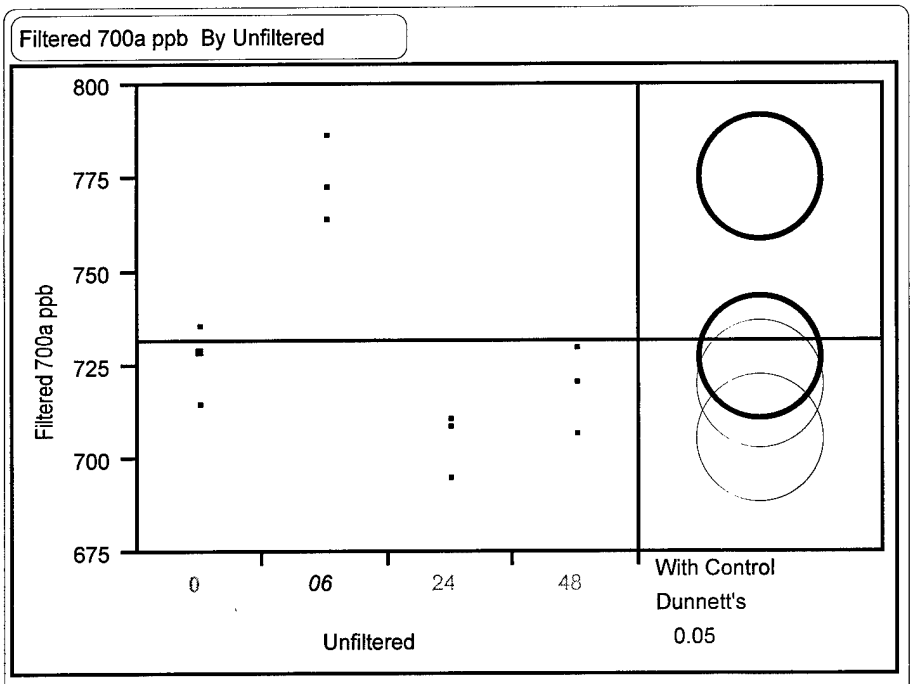
JMP calculated the pertinent values for performing the Dunnett's test. The terminology used by JMP does not coincide with the Appendix B Dunnett's test terminology so the JMP variables are described to explain the Dunnett's test graphs that follow. The critical distance calculated by JMP is identified as the LSD (least significant difference). The absolute difference (Abs(Dif)) is the difference between the control mean and data mean. If the LSD subtracted from the absolute difference [Abs (Dif) – LSD] is negative, the two data are not significantly different. However, if the [Abs (Dif) – LSD] is positive, the two data are significantly different. The three example graphs that follow (Figure 21: Saturation test, Figure 22: Deft and Figure 23: Courtalds) are representative of the display of statistical results of the Dunnett's test comparing each filtered sample to its unfiltered sample.

The chromium concentration replicates for each unfiltered and filtered sample are plotted with mean diamonds. In JMP, the diamonds visually describe the mean and standard deviation. Within the diamond, the mean is the line central to the diamond. The two lines parallel to the mean are one standard deviation above and below the mean. The polygon intersections not touching the mean are two standard deviations above and below the mean.

Also displayed on the graphs are comparison circles. The darkest circle represents the unfiltered mean concentration surrounded by a confidence interval. The circles provide visual confirmation of significant difference as well. If the angle between the intersection of two circles is greater than 90°, the means are not statistically different. If the intersection angle is less than 90° or the circles do not intersect, the means are

statistically different. A summary of the population categorization for each filtered sample is shown in Table 8. Table 9 summarizes the populations assigned to each set of three grouped filtered samples.

Figure 21. JMP Graph: Dunnett's Test Results for a Saturation Limit Test



Means Comparisons

Dif=Mean[i]-Mean[j]	06	0	48	24
06	0.0000	48.0750	55.2697	69.4797
0	-48.0750	0.0000	7.1947	21.4047
48	-55.2697	-7.1947	0.0000	14.2100
24	-69.4797	-21.4047	-14.2100	0.0000

Alpha= 0.05

Comparisons with a control using Dunnett's Method

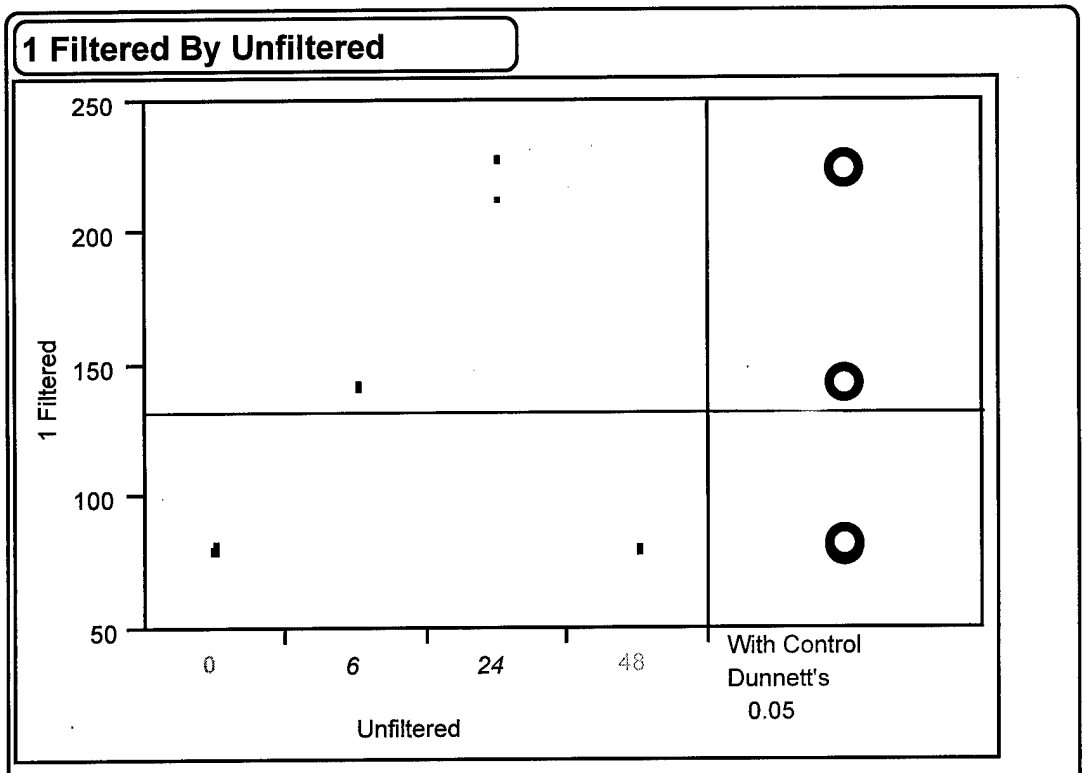
|d|

2.87973

Abs(Dif)-LSD	0
06	23.3478
0	-24.7272
48	-17.5325
24	-3.3225

Positive values show pairs of means that are significantly different.

Figure 22. JMP Graph: Dunnett's Test Results for a Deft Sample



Means Comparisons

Dif=Mean[i]-Mean[j]	24	6	0	48
24	0.000	80.254	141.566	143.291
6	-80.254	0.000	61.313	63.037
0	-141.566	-61.313	0.000	1.725
48	-143.291	-63.037	-1.725	0.000

Alpha= 0.05

Comparisons with a control using Dunnett's Method

|d|
2.87973

Abs(Dif)-LSD	0
24	130.908
6	50.654
0	-10.659
48	-8.934

Positive values show pairs of means that are significantly different.

Figure 23. JMP Graphs: Dunnett's Test Results for a Courtalds Sample

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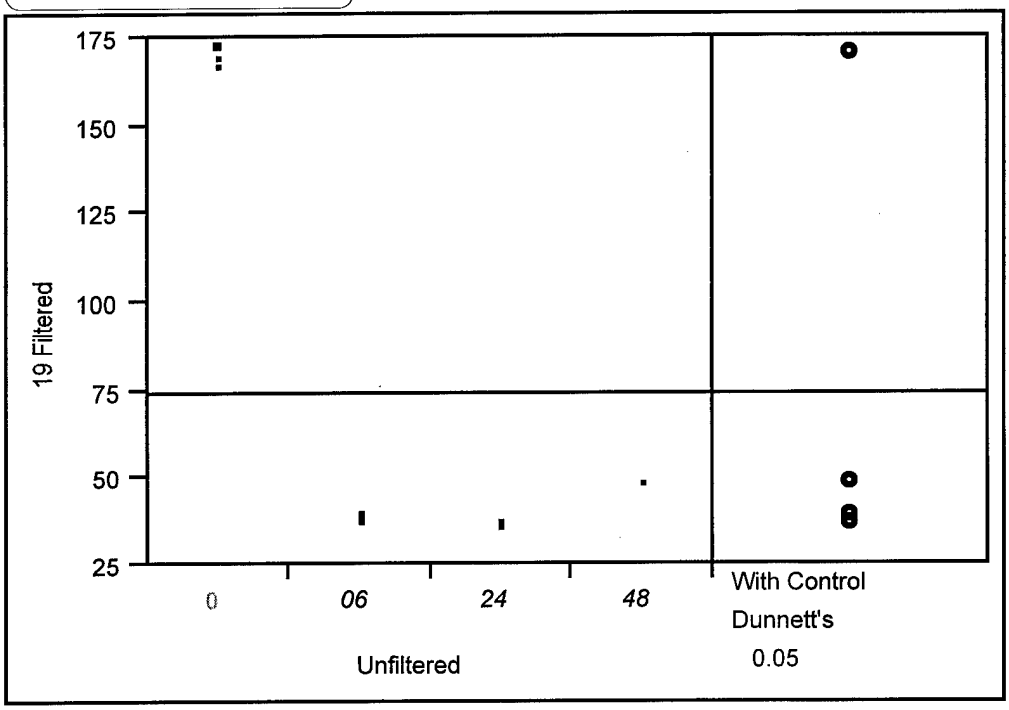

Means Comparisons

Dif=Mean[i]-Mean[j]	0	48	06	24
0	0.000	121.429	130.999	132.866
48	-121.429	0.000	9.570	11.438
06	-130.999	-9.570	0.000	1.867
24	-132.866	-11.438	-1.867	0.000

Alpha= 0.05

Comparisons with a control using Dunnett's Method

|d|

2.87973

Abs(Dif)-LSD	0
0	-3.745
48	117.684
06	127.254
24	129.121

Positive values show pairs of means that are significantly different.

Table 8. Qualitative Summary of Dunnett's Test Statistical Differences

Label	Paint Manufacturer	Filtered after 6 hrs	Filtered after 24 hrs	Filtered after 48 hrs
1	Deft	Type III	Type III	Type II
2	Deft	Type III	Type I	Type III
3	Deft	Type III	Type II	Type II
4	Deft	Type III	Type I	Type II
5	Deft	Type II	Type I	Type I
6	Deft	Type I	Type I	Type III
7	Deft	Type I	Type I	Type I
8	Deft	Type I	Type I	Type I
9	Deft	Type I	Type I	Type I
10	Deft	Type I	Type I	Type I
11	Deft	Type I	Type I	Type I
12	Deft	Type I	Type I	Type I
13	Deft	Type II	Type II	Type II
14	Deft	Type I	Type I	Type I
15	Deft	Type I	Type III	Type III
16	Deft	Type III	Type III	Type II
17	Deft	Type III	Type III	Type II
18	Deft	Type III	Type III	Type II
19	Courtalds	Type I	Type I	Type I
20	Courtalds	Type I	Type III	Type I
21	Courtalds	Type II	Type III	Type III
22	Courtalds	Type III	Type III	Type II
23	Courtalds	Type I	Type I	Type I
24	Courtalds	Type III	Type III	Type III
25	Courtalds	Type II	Type I	Type I
26	Courtalds	Type I	Type I	Type I
27	Courtalds	Type I	Type I	Type I
700a ppb	N/A	Type III	Type II	Type II
700b ppb	N/A	Type II	Type II	Type II
700c ppb	N/A	Type I	Type II	Type II
150a ppb	N/A	Type III	Type III	Type III
150b ppb	N/A	Type III	Type III	Type I
150c ppb	N/A	Type III	Type III	Type III

Table 9. Qualitative Compilation of Statistical Differences Comparing Filtered Samples to Corresponding Unfiltered Sample

	3 Type III	2 Type III 1 Type II	2 Type III 1 Type I	3 Type II	2 Type II 1 Type III	2 Type II 1 Type I	1 Type I 1 Type II 1 Type III	3 Type I	2 Type I 1 Type II	2 Type I 1 Type III
Deft	0	4	2	1	1	0	1	5	1	1
Courtalds	1	2	0	0	0	0	0	4	1	1
Total Paint Samples	1	6	2	1	1	0	1	11	2	2
700 ppb Samples	0	0	0	1	1	1	0	0	0	0
150 ppb Samples	2	0	1	0	0	0	0	0	0	0

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