DEVELOPING A SEQUENTIAL ANALYTICAL PROCEDURE FOR EVALUATING CHROMIUM(III) AND CHROMIUM(VI) SPECIATION AND THEIR DIFFERENTIAL SOLUBILITIES FROM AIR SAMPLES

by

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Abstract

Workplace exposure to chromium species presents significant health risks. While some of the current analytical methods can measure total chromium and Cr(VI) at the threshold limit values (TLV®)s, there remains a need for validated methods that can reliably quantify both Cr(III) and Cr(VI) at 0.1 × TLV® from a single sample to meet WorkSafe BC's goal for enhanced monitoring requirements. This is particularly important for the 2020 ACGIH TLV® of 0.0002 mg/m³ for Cr(VI). A novel sequential analytical procedure was developed for the quantification of soluble Cr(III), soluble Cr(VI), and insoluble chromium species from a single air sample using Disposable Inhalable Samplers (DIS)s. The method combines ion chromatography and inductively coupled plasma mass spectrometry (IC-ICP-MS) with EPA Method 6800 speciated isotope dilution mass spectrometry (SIDMS) to enable precise quantification and correction of species interconversion. An insoluble chromium microwave digestion method was developed using nitric acid, sulfuric acid, and hydrogen peroxide for difficult-to-digest chromium oxides.

Method validation demonstrated detection limits below 0.03 × TLV for soluble chromium species and insoluble chromium. The use of EPA 6800 SIDMS improved method precision for soluble species, with recoveries of 99-109% for Cr(VI) at concentrations ranging from 0.1 to 2 × TLV. The standalone insoluble chromium digestion achieved 90-105% recovery across all concentration levels. Matrix effect studies revealed that soluble iron(III) (Fe(III)) reduced Cr(VI) recoveries to 52-64%, but this interference could be corrected using isotope dilution techniques.

The sequential procedure showed promising results but indicated potential losses during filtration, with insoluble chromium recoveries of 75-80%. This work provides a foundation for chromium speciation analysis that meets current ACGIH exposure limit requirements while reducing analytical costs by eliminating the need for multiple samples.

Keywords: Chromium speciation, hexavalent chromium, trivalent chromium, isotopic tracking, speciated isotopic dilution mass spectrometry (SIDMS), threshold limit value (TLV®)

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List of Abbreviations

American Conference of Governmental Industrial Hygienists	ACGIH
American Industrial Hygiene Association	AIHA
American Society for Testing and Materials	ASTM
Ammonia	NH_3
Ammonium bifluoride	NH_4HF_2
Ammonium nitrate	NH_4NO_3
As low as reasonably achievable	ALARA
Chromium(III) oxide	Cr_2O_3
Coefficient of variation (relative standard deviation)	CV
Dermal sensitization	DSEN
Dichromate ion	$Cr_2O_7^{2-}$
Dionex ICS-5000 Ion chromatography system	ICS-5000
Diphenyl carbazide	DPC
Disposable Inhalable Samplers	DIS
Double deionized	DDI
Environmental Protection Agency	EPA
Ethylenediaminetetraacetic acid	EDTA
European Standard	EN
Health and Safety Executive	HSE
Hexavalent chromium	Cr(VI)
High-performance liquid chromatography	HPLC
High-performance liquid chromatography inductively coupled plasma mass spectrometry	HPLC-ICP-MS
Hydrofluoric acid	HF
Hydrogen peroxide	H_2O_2
Inductively coupled plasma mass spectrometry	ICP-MS
Inductively coupled plasma-optical emission spectroscopy	ICP-OES
Instrument detection limits	IDL
Internation Organization for Standardization	ISO
Ion chromatography	IC
Ion chromatography inductively coupled plasma mass spectrometry	IC-ICP-MS
Ion chromatography ultraviolet spectroscopy	IC-UV
Iron(II) chromite	$FeCr_2O_4$
Fe(III) chloride	$FeCl_3$
Fe(III) oxide	Fe_3O_4
Limit of detection	LOD
Limit of quantification	LOQ
Logarithmic scale of acidity	pH
Manganese ferrite	$Fe_3Mn_3O_8$
Mass-to-charge ratio	m/z

Measure of resistivity	MΩ
National Institute for Occupational Safety and Health	NIOSH
Natural chromium	^{Nat}Cr
Nickel chromite	$NiCr_2O_4$
Nitric acid	HNO_3
Northern Analytical Laboratory Services	NALS
Occupational Health & Safety Regulation	OHSR
Occupational Safety and Health Administration	OSHA
Permissible Exposure Limit	PEL
Logarithmic scale of acidity	PEEK
Polyether ether ketone	pH
Polytetrafluoroethylene	PTFE
Polyvinyl chloride	PVC
Respiratory sensitization	RSEN
Short-term exposure limit	STEL
Speciated isotope dilution mass spectrometry	SIDMS
Speciated isotope dilution techniques	SID
Stainless steel welding fume	SSWF-1
Standard operating procedure	SOP
Sulfuric acid	H_2SO_4
Threshold Limit Value	TLV®
Time-Weighted Average	TWA
Trivalent chromium	Cr(III)
Ultraviolet-visible spectroscopy	UV-Vis
University of Northern British Columbia	UNBC
Volume per volume ratio	v/v
Weight per weight ratio	w/w

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Dedication

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1. Introduction

1.1 Relevance

Chromium is found in more than one valence state, each of which has different properties and toxicities[1–3]. The two most common valence states found in workplace air are trivalent chromium and hexavalent chromium: Cr(III) and Cr(VI), and these compounds can be soluble, sparingly soluble, and insoluble.

Industrial exposure to chromium primarily occurs in three major sectors: metal processing and finishing, chemical production, and manufacturing operations. In metal processing and finishing, workers face significant exposure risks to Cr(VI), while working with stainless steel welding and chrome plating operations[4,5]. The ferrochrome industry presents a unique challenge, as workers may be exposed to both Cr(III) and Cr(VI) species during various production stages[6]. Within the chemical production sector, there are several high-risk processes for chromium exposure. Chromate production facilities primarily handle Cr(VI) complexes, while chrome pigment manufacturing involves handling both Cr(III) and Cr(VI) species, and dye manufacturing entails primarily Cr(III) species[5–8]. In the manufacturing and processing sector, battery production involves Cr(VI) exposure, leather tanning operations involve Cr(III) compounds, and rubber manufacturing requires handling both Cr(III) and Cr(VI) compounds[5,7].

Beyond these industrial sectors, various occupation categories face increased risks of chromium exposure. Construction and maintenance workers; such as, cement workers, abrasive blasting workers, and painters encounter both Cr(III) and Cr(VI)[4,5]. Hot work operations, including welding, cutting, brazing, soldering, and torch work, consistently present a risk of exposure to both chromium species[4,5]. Specialty manufacturing operations present additional exposure scenarios. Candle makers and printers work with materials containing both Cr(III) and Cr(VI) compounds[7]. In equipment maintenance, workers performing copying machine maintenance and handling toner disposal may be exposed to Cr(VI) compounds[7]. Many of these occupations exist throughout British Columbia and Canada, potentially affecting thousands of workers.

One of the main hazards of Cr(III) is its ability to accumulate intracellularly. Cr(III) enters cells slowly, in small amounts, through passive diffusion or phagocytosis, but the back-diffusion is slow in comparison and can lead to an accumulation of Cr(III) within the cells[9,10]. In contrast, Cr(VI) uptake by cells occurs rapidly via anion transport mechanisms. Water-soluble Cr(VI) compounds are highly irritating to the skin and mucous membranes and can cause sensitization of the skin and irritation of the respiratory tract[10]. Cr(VI) is a carcinogen and is toxic to human health, causing lung and sinonasal cancers[1,10,11]. Chromium is intentionally oxidized to Cr(VI) for various industrial applications, including metal finishing (chrome plating, aluminum anodizing), chemical manufacturing (pigments, dyes), tanning, glass making, wood preservation, and specialty coatings (reflective paints)[5–8]. Oxidation of chromium from these industrial applications increases the risk of chromium exposure within these industries[10,11]. Hot working and welding of stainless steel is a common source of Cr(VI) exposure in workplaces[10,11]. Since the health effects of Cr(VI) exposure are severe, Cr(VI) is the overwhelming focus of exposure assessment and control where chromium is encountered. This includes the production of ferrochrome and stainless steel, where, high-temperature processes can oxidize Cr(III) to Cr(VI)[10,11]. Workers can inhale airborne Cr(VI) as dust, fumes, or mist as a result of the production of chromate pigments, dyes, and powders (such as chromic acid and chromium catalysts); working near chrome electroplating; performing hot work and welding on stainless steel, production of high chrome alloys and chrome-coated metal; and application and removal of chromate-containing paints and other surface coatings. Inhalation exposure may cause lung cancer, irritation or damage to the nose, throat, and lungs, and as many as 104,000 workers in Canada are exposed to Cr(VI) in the workplace[10,12]. In 2023, 3900 individuals in British Columbia were working in clothing manufacturing, leather manufacturing, and allied product manufacturing. Approximately 3900 printers or individuals were working with toners and copying ink, and 11,900 workers were working in the fabricated metal product manufacturing industry[13]. With advancements in technology and industrial processes, the number of people at risk to exposure of Cr(VI) continues to climb.

In the United States, the Occupational Safety and Health Administration (OSHA) regulatory agency enforces Permissible Exposure Limits (PEL)s for airborne Cr metal and insoluble salts of 1 mg/m^3 (measured as Cr), Cr(III) compounds of 0.5 mg/m^3 (measured as Cr) and Cr(VI), measured as Cr(VI), of 0.005 mg/m^3 expressed as a time weighted average over a typically 8-hour work-shift[10]. In addition, OSHA enforces an Action Level concentration, also expressed as an 8-hour time-weighted average, in which an employer is required to undertake specific actions for Cr(VI) of 0.0025 mg/m^3. OSHA states, "When monitoring for Cr(VI), employers must use a method of monitoring and analysis that provides values within plus or minus 25 percent of the true value at least 95 percent of the time for airborne concentrations at or above the Action Level."[11]. OSHA outlines various examples of methods that meet the outlined criteria; such as, OSHA method ID215 (version 2) and the US National Institute for Occupational Safety and Health (NIOSH) methods 7600, 7604, 7605 and 7703[14–17]. In 2018, the American Conference of Governmental Industrial Hygienists (ACGIH®) published new/revised limits for Cr compounds. In 2020, the ACGIH recommendations for inhalable 8-hour Time-

Weighted Average Threshold Limit Values (TLV®) are 0.5 mg/m^3 for metallic Cr, measured as Cr, 0.003 mg/m^3 for Cr(III) compounds measured as Cr(III), and 0.0002 mg/m^3 for Cr(VI) compounds measured as Cr(VI) [10,18]. In addition, ACGIH recommends a 15-minute TWA short-term exposure limit (STEL) for Cr(VI) compounds of 0.0005 mg/m^3. These TLVs are intended to represent concentrations to which, during an 8-hour workday and a 40-hour work week, workers may be repeatedly exposed every day for a working lifetime without adverse effects. However, ACGIH acknowledges that its TLVs are not consensus standards and do not consider economic or technical feasibility issues[11]. Since these limit values are substantially lower than those for which OSHA and NIOSH were developed and validated, methods that can be shown to address these lower limits are needed. A fundamental difference between the OSHA and ACGIH limit values is that OSHA collects air samples using a sampler for "Total Particulate Matter" while ACGIH recommends using a sampler that meets the ISO "Inhalable" sampling convention[19]. Both Cr(III) and Cr(VI) have respiratory sensitization (RSEN) and dermal sensitization (DSEN) notations for the water-soluble compounds[11]. This indicates that the water-soluble forms of Cr(III) and Cr(VI) can potentially cause allergic reactions in the respiratory system and skin. Under the current BC Occupational Health & Safety Regulation (OHSR), both Cr(III) and Cr(IV) are considered sensitizers and exposure to these substances should be kept "as low as reasonably achievable" (ALARA)[18].

The goal of this research is to develop a procedure for air sampling and analysis of Cr species to meet the ACGIH recommended exposure limits, which can assist the WorkSafe BC Exposure Limit Review Committee's ability to recommend new, revised, and more protective TLVs for Cr(III) and Cr(VI) as regulatory BC exposure limits. Those responsible for safeguarding the health and well-being of workers, including occupational hygienists involved with corporations, trade~~s~~ unions, and regulators will benefit from demonstration of adherence to exposure limit guidelines and standards and would also benefit from the development of this sequential extraction procedure for Cr(III) and Cr(VI) since it would eliminate the need to collect multiple samples in occupations where both species are present, thereby bringing down sampling costs. With adherence to the limit guidelines and provision of a safe workplace, the employer and the related industries will grow in their efforts to support a safe workplace.

1.2 Project Description

While some chromium speciation methods exist, the most promising is IC-ICP-MS because it offers superior sensitivity and selectivity and can be used in conjunction with SID methods. The objective of this research is to develop a novel procedure capable of quantifying water-soluble chromium species Cr(III) and Cr(VI) in a single air sample using EPA 6800 SIDMS with IC-ICP-MS that can provide a solution towards meeting the adopted ACGIH TLVs for Cr species. This allows for tracking and correction of interconversion between the chromium species.

Though inherent challenges are associated with SIDMS, such as, minimizing polyatomic interferences, interconversion, and limitations in linear range and mass bias, several strategies can be employed to overcome them. These strategies include utilizing the helium collision mode on the ICP-MS, incorporating an ammonium nitrate buffer solution, and applying appropriate mass bias laws to achieve the desired sensitivity level.

Polyvinyl chloride (PVC) Disposable Inhalable Samplers[20] (DIS) were evaluated for method validation. Prior to use, the filters were purchased pre-cleaned using hydrogen peroxide to reduce Cr content[21]. The support pad of the capsule featured a hydrophobic fritted pad to prevent premature passage of the extraction solution through the insert. Furthermore, the extraction process was carried out directly in the DIS sampler, eliminating potential losses of the analyte on the sampling cassette wall (wall-deposits). Subsequently, pH 3 ammonium nitrate extraction solution and monoisotopic standards (EPA 6800) were added to the samples, followed by shaking for one hour and vacuum filtration. The soluble extracts were then subjected to analysis using IC-ICP-MS. Meanwhile, the DIS capsule and remaining particles were subjected to microwave digestion to determine the content of insoluble chromium.

1.3 Research Objectives

The primary goal of this project is to develop and validate an accurate analytical method that can quantify both soluble Cr(III) and Cr(VI) and total chromium in a single inhalable air sample, to address the lack of a validated sampling and analysis method for multiple Cr species in a single sample, at and around the new/revised airborne concentrations recommended by the ACGIH as limits for the airborne inhalable fraction of aerosol. The project also intends to determine the most suitable analysis method for implementation at UNBC-NALS, extending its benefits to Northern BC communities and beyond.

The anticipated outcome of this research is that UNBC-NALS will establish a novel procedure capable of identifying and quantifying different Cr valence states in a single air sample, aligning with the new/revised 2020 ACGIH TLVs. This unified method offers the advantage of replacing the need for three separate samples.

2. Literature Review

2.1 Analytical Challenges

The accurate determination of Cr(III) and Cr(VI) in workplace air presents multiple analytical challenges throughout the sampling, preservation, sample preparation, and measurement phases. These challenges primarily arise from the complex behaviour of chromium compounds and their interactions with various environmental factors.

2.1.1 Species Stability and Interconversion

Chromium exists predominantly as Cr(III) and Cr(VI) but interconversion between the two species is common. In certain situations, such as welding, multiple chromium species can manifest simultaneously in a single sample. Interconversion rates are strongly dependent on pH and matrix composition. The primary forms of Cr(VI) include H_2CrO_4, $HCrO_4^-$, CrO_4^{2-} or $Cr_2O_7^{2-}$, depending on pH[22,23]. From pH $HCrO_4^-$ is the predominant form of Cr(VI). Cr(III) exists as Cr^{3+} at pH less than 3, $CrOH^{2+}$ and $Cr(OH)_2^+$ from pH 3 to 7, and $Cr(OH)_3$ in neutral to basic conditions[22,23]. Under strongly acidic environments ($pH < 3$), Cr(VI) can be reduced to Cr(III)[22,23]. Alkaline environments ($pH > 9$) stabilize the Cr(VI) but risk Cr(III) precipitation[22,23]. It has been previously demonstrated that Cr(III) can be oxidized to Cr(VI) during alkaline digestion, however, only the dissolved forms of Cr(III); such as, the hydroxochromate ion ($[Cr(OH)_4]^-$), are susceptible to oxidation[24,25]. This oxidation can be minimized through hydrolytic destabilization of $[Cr(OH)_4]^-$ by using magnesium hydroxide precipitate[24,25].

2.1.2 Matrix Effect and Reducing Agents

The presence of electron donors, in particular iron or aluminum compounds, plays a key role in chromium interconversion. Aluminum, Fe(II), and Fe(III) are good electron donors, which allows them to easily reduce Cr(VI) to Cr(III). The predominant forms of iron in welding

fumes are Fe_3O_4, $Fe_3Mn_3O_8$ and $FeCr_2O_4$ [26]. The interconversion of the two species poses significant challenges in accurately measuring the chromium species.

2.1.3 Sampling and Collection Efficiency

Traditional sampling methods using cassettes lend to significant challenges due to internal wall deposits. Wall deposits refer to any material that is maintained on the inside wall of the sampling body that does not land on the filter. This can cause an underestimation of 10-60% of the total sample mass[27]. The extent of wall deposits depends on the particle size distribution, air velocity, sampling time, and cassette orientation[27]. Larger particle size is correlated with an increase in wall deposits[27]. For particles greater than 10 μm, inertial deposition leads to deposits primarily near the inlet[27]. Particles less than 1 μm have minimal wall loss due to efficient aerodynamic transport to the filter[27]; however, particulates between 1 to 10 μm, suffer from the combined effects of gravitational settling and turbulent deposition, leading to losses of 25-35% of the collected mass[27].

2.1.4 Analytical Method Limitations

When assessed in air or other environmental samples (i.e. soil and water), chromium is commonly measured by inductively coupled plasma-optical emission spectroscopy (ICP-OES) or mass spectrometry (ICP-MS) with detection limits of 0.1-1 μg/L. The results reflect total chromium as the sum of both Cr(III) and Cr(VI) oxidation states. As the determination of total chromium content in a sample does not differentiate the proportion that is hexavalent, several standardized methods have been developed specifically for the determination of Cr(VI) in workplace air samples (Table 1).

Table 1: Comparison of Standard Methods for Determining Cr(VI) in Workplace Air Samples and the working range based on a 960 L air volume (8-hour sampling at 2 L/min)

Standard Method	LOD (µg/filter)	Working Range	
		µg/filter	µg/m^3
NIOSH 7703[16]	0.08	1-400	1-417
NIOSH 7600[15]	0.05	0.2-7	0.2-7
NIOSH 7605[14]	0.02	0.05-20	0.05-21
ISO 16740[28]	0.01	0.1-10	0.1-10
ASTM D6832[29]	0.01	0.1-10	0.1-10

Ion chromatography (IC) with post-column derivatization with 1,5-diphenylcarbazide (DPC) and UV-Vis detection at 540 nm is the most widely used analytical method for the determination of Cr(VI)[25,30]. While a sequential soluble and insoluble Cr(VI) method has been developed and standardized in ASTM D6832, the ASTM standard does not provide information about the soluble Cr(III) composition[29,30]. Furthermore, speciation methods must strive to preserve the original species distribution, must have sufficient sensitivity (LOD <0.03 x TLV), and have minimal sample preparation to reduce potential contamination, and acceptable measurement uncertainty (RSD <20%).

2.1.5 Method Development Requirements

Industrial work environments, as indicated above, promote chromium species interconversion. The ideal method to detect soluble Cr(III) and Cr(VI) would include the sampler internal wall deposits using an in-capsule extraction for water-soluble chromium compounds and whole-capsule digestion for total chromium. The method must have low detection limits, high selectivity, and minimal species interconversion while being inexpensive, robust, and easy to use [23,31–33]. Workplaces would benefit from a universal, standardized and streamlined method where Cr(VI) exposure and environmental conditions present a risk of particulates coming into contact with high temperatures, acids or bases, and aqueous solutions. This method may not be required by all industries handling chromium-containing agents due to the environmental conditions and starting chromium materials.

2.2 Analytical Methods for Soluble Chromium Speciation

The three most common analytical methods for analyzing the chromium species include ion chromatography ultraviolet spectroscopy (IC-UV), high-performance liquid chromatography inductively coupled plasma mass spectrometry (HPLC-ICP-MS), and ion chromatography inductively coupled plasma mass spectrometry (IC-ICP-MS).

Ion chromatography (IC) is the most common method used for chromium speciation as it provides a means for chemically separating Cr(III) and Cr(VI)[34–36]. The procedures outlined by NIOSH 7605, EPA Method 218.7, and ISO 16740 are recognized methods employed to extract hexavalent chromium from samples, including UV-Vis analysis to detect Cr(VI)[14,28,34]. IC-UV is the easiest method to use, as it involves the separation of the chromium species by IC in a column, followed by post-column complexation with DPC and analysis by ultraviolet spectroscopy at 540 nm[14,23,31,32,35]. EPA Method 218.7 and NIOSH 7605 describe IC-UV determination of Cr(VI) and Cr(III); however, the drawbacks to these methods exclude them from part-per-trillion level quantification[14,35]. There are many different interferences due to other metal ions forming coloured complexes with DPC and other organic matter absorbing light at the same wavelength[14,23,31,32,35]. Furthermore, the detection limits offered are only in the µg/L range[14,23,31,32,35].

HPLC-ICP-MS is a relatively easy-to-use and low-cost method. However, the large eluate volume poses a challenge as the low levels of chromium are often overshadowed by the eluent interferences[37]. Traditionally, HPLC pumps were made of parts containing chromium. This can lead to eluent contamination and a background level approximately seven-fold larger than IC-ICP-MS[33,38]. Newer models of HPLC systems may use polyether ether ketone (PEEK) pumps, offering a metal-free flow path. In comparison, it is much more common for IC systems to be equipped with pump heads and tubing constructed from PEEK, thereby reducing chromium contamination from the eluent. When deciding between HPLC-ICP-MS and IC-ICP-MS, consideration should be made regarding the upfront cost of HPLC and the maintenance requirements. IC is generally less expensive to run and maintain when compared to HPLC.

IC-ICP-MS is the leading method for chromium speciation at the ultra-trace level. The main advantage of IC-ICP-MS methods is that it offers high sensitivity, a wide linear detection range, and can quantify different isotopes simultaneously. The IC serves to separate Cr(VI) and Cr(III) by passing the sampling and the eluent through an ion exchange column[25,33,37–42]. For workplace air samples, standardized methods specify an ammonium sulfate/ammonium hydroxide buffer (pH 8) to prevent species interconversion, while environmental water analysis may employ dilute nitric acid[29,30,43]. The column outlet is then directly connected to the nebulizer of the sample introduction system of the ICP-MS[37,38]. The effluent is then atomized by the plasma torch, passed through a nickel-tipped with copper base sampler cone, then through a nickel skimmer cone, and enters the collision cell, where ions of unwanted mass-to-charge (m/z) ratios will be ejected and not reach the detector[37,38].

The application of speciated isotope dilution techniques (SID), described in EPA Method 6800, to IC-ICP-MS allows for the determination and correction of species interconversion[39,44,45]. This tandem technology is referred to as SID-MS. Samples are spiked with a known amount of the two of the most abundant isotopes of chromium, ^{50}Cr (4.35%) and ^{53}Cr (9.50%)[3,28]. Four different isotope ratios, ^{50}Cr(III)/^{52}Cr(III), ^{53}Cr(III)/^{52}Cr(III), ^{50}Cr(VI)/^{52}Cr(VI), and ^{53}Cr(VI)/^{52}Cr(VI) are then determined and extrapolated to determine the amount of interconversion and the corrected concentration of Cr(VI) and Cr(III) in the sample[23,25,31,38–41]. In EPA 6800, SID-MS was demonstrated to correct 80% of Cr(VI) reductions, potentially attaining a 90% correction rate[39]. As the method relies on changes in the known spiked concentrations of isotopic species at the time of collection, it can also act as a diagnostic tool between different methods and various steps from sampling, digestion, and extraction. Specifically, IC-ICP-MS used according to EPA 6800 speciated isotope dilution mass spectrometry (SIDMS) can correct for interspecies conversion that results from sampling and extraction, reducing false positives due to Cr(III) oxidation to Cr(VI)[24,25], and reducing false negatives, as a result of Cr(VI) reduction to Cr(III). SIDMS, based on EPA 6800, shows great promise and merits further investigation[31,39].

Pioneering work by Tirez et al. established foundational methods for investigating Cr(III) and Cr(VI) interconversion using SIDMS coupled with IC-ICP-MS[44,45]. Their initial method achieved detection limits of 0.8 ng/mL for Cr(VI) using a NaOH eluent and demonstrated recoveries of 90-110% for Cr(VI) spikes in alkaline digestions[45]. Tirez et al. identified that 2% of the ^{53}Cr(VI) enriched spike was present as ^{53}Cr(III), indicating that mathematical corrections were required in the SIDMS equation[45]. In a 2011 ambient air study by Tirez et al., it was observed that 1.7% of Cr(III) was oxidized during alkaline extraction which could cause false positives[44]. During this study, it was noted that Cr(VI) and Cr(III) spikes remained stable on impregnated filters after 16 hours of sampling. However, the presence of iron(II) contributed to Cr(VI) reduction[44].

While the use of SID-MS has previously been used in environmental applications, such as soil and water analyses, it has yet to be fully validated for use in an industrial hygiene setting[25,46]. From its application to environmental samples, a few challenges have been identified. These challenges include polyatomic interference (or mass interferences), which are inherent to ICP-MS, minimizing interconversion, and limitations in the linear behaviour of SID-MS.

Polyatomic interferences result from multiple isotopes of different elements combining while in the plasma of the ICP-MS[23,31,32]. The most common interferences are $^{40}Ar^{12}C^{+}$, formed from the argon gas in the ICP-MS reacting with carbon atoms, and chloride interferences. These interferences have a m/z ratio of 52. This interferes with the measurement of ^{52}Cr (m/z= 52), resulting in a higher background reading for ^{52}Cr [23,31,32]. If the interference concentration changes between samples, this will also result in a positive bias. Polyatomic interferences can be addressed using collision reaction cell techniques. The ICP-MS can be set to helium collision mode, which floods the collision chamber with helium gas. This will induce the dissociation of the polyatomic species, which can then be rejected by the mass analyzer. Additionally, using a lower flow rate for the IC eluent will allow for better separation of the chloride interference from the chromium species[23,31,32]. With the separation of the chloride interference, the chloride ions will not reach the detector at the same time as the chromium species.

Interconversion between Cr(VI) and Cr(III), while not entirely preventable, can be minimized through pH optimization and the use of chelating agents. While most environmental applications have added ethylenediaminetetraacetic acid (EDTA) to solid sample extracts for SIDMS, EDTA should be avoided if possible[23,31,39]. Due to the poor solubility of EDTA at pH<8, it is often preferred to use the EDTA disodium salt. The EDTA disodium salt can cause polyatomic interference due to high carbon composition and is prone to sodium salt deposition on the cone orifice of the ICP-MS[23,31,39]. The salt deposition produces unnecessary wear and tear on the ICP-MS, resulting in extensive maintenance, increased downtime, equipment replacement and increased associated costs[23,31]. EDTA can potentially be replaced with an ammonium nitrate buffer adjusted to pH 3 to 4. Furthermore, the advantage of ammonium nitrate is that it will not cause salt build-up in the ICP-MS[32,33], thereby reducing maintenance on the ICPS-MS. Under acidic conditions, high redox potential favours the formation of Cr(III) complexes. Under alkaline conditions, the redox potential decreases and favours the formation of Cr(VI) complexes. At pH 4, there is minimal degradation of Cr(VI) to Cr(III) due to low redox potential[22]. Higher pH solutions would favour the precipitation of Cr(III) as $Cr(OH)_2$; however, at pH 4, Cr(III) forms soluble hexacoordinate complexes with water and Cr(VI) is in the form of dichromate ($Cr_2O_7^{2-}$) [22]

While SID-MS is useful for tracking and correcting chromium species interconversion, it should be noted that the isotope ratio is not necessarily a linear relationship with the amount ratio of the analyte and the spike[32,39]. The relationship is typically hyperbolic, but it can be approximated as linear in the absence of isobaric interferences[23,31,37]. Mass bias occurs when ions of different masses are passed through the mass spectrometer with different efficiencies[23,31,37].

Mass bias laws can be applied in most cases. A linear mass bias law can be applied for up to three decimal places[23,31,37].

2.3 Analytical methods for insoluble chromium

Several analytical methods are available for determining insoluble chromium in workplace air samples, including NIOSH 7303, NIOSH 7304, and ISO 15202[47–49]. NIOSH 7303 involves the addition of nitric acid and hydrochloric acid, followed by heating to 95°C on a hot block[47]. NIOSH 7304 entails adding nitric acid to the sample and performing microwave digestion at 220°C [48]. Microwave digestion is generally considered a more robust method as it allows for higher temperatures and pressures, increasing the likelihood of complete sample digestion. ISO 15202 describes various hot block and microwave extraction procedures for metal analysis in workplace air[49].

The primary challenge in establishing a digestion procedure for insoluble chromium on DIS capsules is ensuring complete digestion of the DIS capsule and chromium compounds. In stainless steel welding fumes like SSWF-1 (HSE Gov), chromium comprises 8.4% of the total sample mass and is primarily present as a spinel-oxide dominant crystalline phase[50]. Spinel-oxide structures are often difficult to digest and require microwave digestion procedures for complete digestion. Chromium oxides typically exhibit a spinel-oxide structure, which is difficult to digest. Previous studies have demonstrated that microwave digestion using nitric acid, hydrochloric acid, and hydrofluoric acid at 180°C (Annex G ISO 15202-2) is suitable for digesting spinel oxide materials[49,50].

2.4 Sequential Analytical Methods

Sequential soluble and insoluble Cr(VI) methods have been validated on workplace air samples. Key developments include ASTM D6832[29] and ISO 16740[28] with supporting performance data by Ashley et al. (2009)[30]. ASTM D6832 describes a two-stage sequential extraction process with analysis using DPC and UV-Vis[29,30]. The first stage extracts soluble Cr(VI) by soaking the filter for 1 hour in either water or 0.05 M ammonium sulfate/0.05 M ammonium hydroxide buffer solution[29,30]. This could be done in either a separate container or as an in-cassette extraction to incorporate wall deposits[29,30]. Following the extraction, particulates are moved through filtration or centrifugation, and the solution pH is adjusted to 8.0 using 2 M ammonium sulfate/1 M ammonium hydroxide before diluting to a predetermined volume[29,30].

The second stage of the sequential procedure addresses insoluble Cr(VI) compounds. This extraction procedure requires the addition of 10 mL of 2% (m/v) sodium hydroxide/2% (m/v) sodium carbonate (pH 13) to the sample. The samples are then heated on a hot plate at 135°C for 60 to 90 minutes, followed by quantitative dilution and filtration of any remaining particulates[29,30].

The choice between performing the sequential extraction versus the single extraction depends on the expected sample composition[29,30]. Welding fumes typically require sequential analysis due to the presence of both soluble and insoluble species. In contrast, chrome plating samples containing primarily soluble Cr(VI) may only require the soluble extraction step[29,30]. The method demonstrates a working range of 0.01 to 10 µg, corresponding to 0.1-100 µg/m^3, assuming 1 m^3 air volume[29,30]. Soluble Cr(VI) recoveries were 94-122% when extracted with water and 98-104% when extracted with ammonium sulfate/ammonium hydroxide[29,30].

3. Materials and Methods

3.1 Materials and Equipment

3.1.1 Reagents and Standards

Double deionized (DDI) water (18 MΩ cm^{-1}), prepared from a Milli-Q IQ 7000 Ultrapure Water purification system (Molsheim, France), was used for the preparation of all solutions throughout this study. A 0.06 M NH_4NO_3 (pH 3, buffer capacity 0.001 mol L^{-1} pH^{-1}) extraction solution was prepared by dissolving 9.60 g NH_4NO_3 (99.999% trace metals basis, Aldrich, St. Louis, MO, USA) and 50 µL HNO_3 in 2 L DDI water. Concentrated HNO_3 (70%) (Aristar® Plus Trace Metals Basis, BDH, Radnor, PA, USA) was used to prepare a 0.4 M HNO_3 mobile phase for the IC-ICPMS. Concentrated HNO_3, H_2SO_4 (Aristar® Plus, BDH, West Chester, PA, USA) and H_2O_2 (ULTREX® II, Ultrapure for trace metal analysis, J. T. Baker, Radnor, PA, USA) were used for the microwave digestion of the DIS capsule.

Four reference stock solutions from Applied Isotope Technologies (Pittsburgh, PA, USA) were used to prepare subsequent dilutions for spiking and calibration, including $^{nat}Cr^{3+}$ standard, 126.0422 µg/g 1% HNO_3; $^{nat}Cr^{6+}$ standard, 101.6977 µg/g in DDI water; $^{50}Cr^{3+}$ spike, 99.9915 µg/g in 1% HNO_3; $^{53}Cr^{6+}$ spike, 100.7669 µg/g in 1% NH_3 (aqueous). $^{50}Cr^{3+}$ spike solution was prepared from ^{50}Cr-enriched metal (Lot No. CR02192019B). $^{53}Cr^{6+}$ spike solution was prepared from ^{53}Cr-enriched oxide (Lot No. CR03282019B). The isotopic abundances of the natural and isotope-enriched chromium standards are reported in Table 2. In addition, a Cr^{3+} standard, 100.00 µg/mL in 2% HNO_3 (Inorganic Ventures, Christiansburg, VA, USA) and a Cr^{6+} standard, 100.01 µg/mL in DDI water (Inorganic Ventures, Christiansburg, VA, USA) were used to accommodate the higher concentration spikes of the natural abundance Cr^{3+} and Cr^{6+}.

Table 2: Isotopic Composition of Chromium Standards from Applied Isotope Technologies.

Isotopic Abundance	**^{Nat}Cr(III)**	**^{Nat}Cr(VI)**	**^{50}Cr(III)**	**^{53}Cr(VI)**
^{50}Cr (%)	4.345	4.345	96.05	0.01
^{52}Cr (%)	83.789	83.789	3.66	2.65
^{53}Cr (%)	9.501	9.501	0.24	97.20
^{53}Cr (%)	2.365	2.365	0.05	0.12
Total (%)	100.00	100.00	100.00	99.98

3.1.2 Reference Materials

A stainless steel welding fume (SSWF-1) reference material (HSE Gov, Buxton, DB, UK), Cr_2O_3 (Alfa Aesar, Mississauga, ON, Canada), and $NiCr_2O_4$ (Alfa Aesa, Ottawa, ON, Canada) were used as reference materials to assess the success of the microwave digestion process.

3.1.3 Sampling Media

PVC DIS capsules, purchased from Zefon Scientific, were selected as the sampling media. The DIS capsules were pre-cleaned using hydrogen peroxide to reduce background chromium content by High Purity Standards[21]. Each DIS body contained a hydrophobic fritted support pad. The hydrophobic nature of the PVC filter and support pad enabled direct in-capsule extraction, thus minimizing analyte losses from wall deposits in the sampling cassette.

3.1.4 Instrumentation

A Secura 225D-1S balance (Sartorius), capable of weighing to ± 0.00001 g, was used to weigh samples, reference materials, standards, and dilutions.

Filtration of the soluble extract was performed using a Supelco VISIPREP vacuum manifold with 3D-printed nylon carbon fiber DIS filter funnels. The DIS filter funnels were designed based on a Buchner funnel. The diameter was slightly larger than the DIS capsule, and the funnel had threads to connect to the vacuum manifold directly. When filtering the samples, the DIS capsule and the sampler body inlet would be placed on the DIS filter funnel to minimize contamination and create a good vacuum seal. The DIS filter funnel (

Figure *1*) was designed in Fusion 360 through collaboration with Ahmad Jalil and SparkLab.

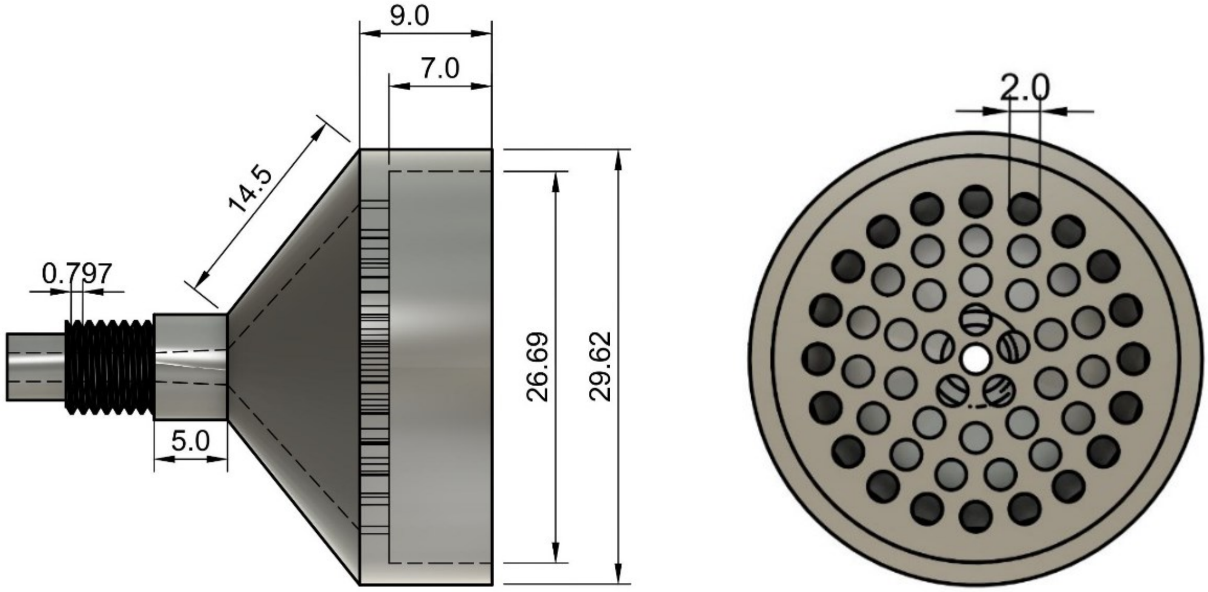


Figure 1: Filter funnel design for 25 mm DIS with side view (left) and top view (right) designed in Fusion 360.

A Dionex ICS-5000 ion chromatography system equipped with an IC5 series autosampler and a Dionex IonPac AG7 (50 mm x 4 mm, 10 µm) (PEEK) guard column was used for separating Cr(III) and Cr(VI). The outlet of the column was directly interfaced with the nebulizer of the ICP-MS (7500 Series ICP-MS, Agilent Technologies) using a piece of PEEK tubing. A custom automation system was developed to enable communication between the IC and ICP-MS computers since direct communication could not be established through pin connections. The system consisted of two networked computers connected via a dedicated network switch, operating in a closed loop without external internet access. Computer A (connected to the IC) was programmed to monitor for specific visual triggers indicating completed chromatographic runs, while Computer B (connected to the ICP-MS) executed predefined automated responses to initiate data collection. This setup enabled seamless integration between the two instruments while maintaining system security. The automation system was developed in collaboration with Ahmad Jalil.

Preliminary studies for the insoluble chromium method were done using a DigiPrep MS block digester system (SCP Science), a Multiwave 5000 with 8NXF100 rotor (Anton Parr, demo unit) and a MARS6 microwave digestion system. The final method development was performed using a MARS6 microwave digestion system (CEM) equipped with iWave temperature feedback control and iPrep 12 (100 mL) vessels. After establishing the CEM method, NIOSH 7304 was also evaluated on the MARS6 system as a potential simplified alternative, though it proved unsuccessful. This is most likely because nitric acid alone was not a strong enough oxidizer to fully digest the spinel chromium compounds. Preliminary method development samples were analyzed using a 5100 series ICP-OES (Agilent Technologies), while the final validated method used a 7500 Series ICP-MS (Agilent Technologies) for analysis.

3.2 Method Development Strategy

The search strategy involved a systematic literature review to identify relevant ISO, NIOSH, and EPA methods pertaining to metals in workplace air, soluble chromium, and insoluble Cr. The initial focus was on examining existing ISO 15202, NIOSH 7304, and EPA Method 6800, which discuss sampling methods, sample handling, wall deposits, method validation, measurement uncertainty, and microwave digestion procedures. EN ISO 21832 was identified as the foundational source for method validation for this project[51]. The insoluble chromium microwave digestion procedure was developed starting from NIOSH 7304, while EPA Method 6800 was the basis for incorporating the tracking of interconversion during sample extraction and analysis.

The selection of the extraction solution for soluble Cr(VI) and Cr(III) compounds was based on a literature review of the solubility of chromium at various pH values and the compatibility of the extraction solution with the ICP-MS. Additionally, a method application note for chromium speciation in drinking water was the starting point for developing the preliminary conditions for the IC-ICP-MS analysis.

The inclusion of literature used to develop the method, and the validation plan was restricted to peer-reviewed journals and methods. Application notes developed by instrument manufacturers were included with the caveat that the results were supported by other sources of peer-reviewed work.

3.3 Development of Soluble Chromium Method

3.3.1 Preliminary Method Development

The initial method development focused on three key areas: chromatographic separation, signal optimization, and interference reduction. While established methods like ASTM D6832[29] specify an ammonium sulfate/ammonium hydroxide buffer (pH 8) for the extraction of soluble Cr(VI), this study utilized an alternate approach based on specific analytical considerations. The chosen method was derived from a Thermo Scientific application note[43] using 0.06 M ammonium nitrate (pH 3). This approach balances two competing analytical requirements: EPA 6800 specifies acidifying the samples to pH 1.7 to 2 for chromatographic separation; whereas, pH values below 3 significantly increase the risk of Cr(VI) to Cr(III) reduction. The pH 3 value represents a compromise that minimizes species interconversion while maintaining chromatographic separation. An additional consideration for deviating from ASTM D6832 was the potential for increased wear and tear on the ICPMS when using ammonium hydroxide due to the risk of salt deposition that would then incur increased maintenance and costs, and lead to increased background signal for m/z 52 due to the formation of $^{36}Ar^{16}O^{-}$.

Separation of soluble Cr(VI) and Cr(III) was performed using a 0.4 mol/L nitric acid mobile phase with both a Dionex IonPac AG7 guard column and Dionex IonPac AS7 as specified in the Thermo Scientific application note[43]. Initial testing revealed that using both columns resulted in diminished peak intensity due to the extended 10-minute run time required for separation. Sole use of the AG7 guard column allowed for run time to be reduced to 5 minutes while continuing to maintain sufficient separation of Cr(VI) and Cr(III) species.

To optimize detection sensitivity, dwell times of 0.1, 0.5, 0.6, and 0.75 seconds were evaluated along with sample loop sizes of 50 µL, 250 µL, and 1000 µL. A dwell time of 0.75

seconds combined with a 1000 μL sample loop provided the highest signal-to-noise ratio without compromising chromatographic resolution.

A significant interference with the Cr(VI) peak was observed during the initial method development. To investigate potential sources of this interference, several tests were conducted comparing: uncleaned DIS filters, uncleaned DIS filters with 5 minutes of airflow at 2 L/min, cleaned DIS filters, cleaned DIS filters with 5 minutes of airflow, cleaned filters extracted in DDI water-rinsed DIS bodies, and cleaned DIS filters washed three times with DDI water. These tests aimed to determine whether the interference originated from the filter material, air sampling process, or DIS body contamination. To minimize the observed interference, the helium collision gas flow was systematically evaluated at 0, 1, 2, 3, and 4 mL/min. A flow rate of 3 mL/min provided optimal interference reduction while maintaining acceptable sensitivity for both chromium species.

3.3.3 Final Soluble Chromium Species Extraction Procedure

Cleaned DIS capsules were spiked with a 0.1:1 up to 10:1 molar ratio of ^{50}Cr(III) to ^{52}Cr(III) and ^{53}Cr(VI) to ^{52}Cr(VI) using chromium stock solutions and the enriched isotope standards. The DIS capsules were placed in DIS sampler bodies, and then 2.5 mL of 0.06 M ammonium nitrate was added to the DIS. The DIS lid was closed, and the samples were shaken at room temperature for 1 hour. The DIS capsule was removed from the sampling body, and the extract was filtered through the DIS filter body. The filtered extract was then diluted 12-fold using 0.06 M ammonium nitrate. This dilution factor was chosen to accommodate running the same sample multiple times on the IC-ICP-MS as per Table 3, with a minimum sample volume requirement of 6 mL. The DIS capsules were then rinsed three times with DDI water, and the rinse was discarded before the insoluble extraction. The rinsing removed any soluble chromium solution that may not have been collected initially to prevent it from creating a positive bias in the insoluble digest.

Table 3: IC-ICP-MS conditions used in method validation for soluble Cr(VI) and Cr(III) on DIS capsules

Dionex ICS-5000	
Column	Dionex IonPac AG7 (50 mm x 4 mm, 10 µm) (PEEK)
Flow Rate	1 mL/min
Column Heater	30˚C
Eluent	0.4 M HNO_3 (pH 3)
Sample Loop	1000 µL
Agilent 7500 ICP-MS	
Spray Chamber	Quartz, Scott double-pass
Nebulizer	Ezylok Micromist
Sampler Cone	Agilent Nickel
Skimmer Cone	Agilent Nickel
Acquisition Mode	Time-Resolved Analysis
Flow Gas	Plasma 15 L/min
Power RF	1500 W
Reaction Gas	3 mL/min He
Analytical Masses	^{50}Cr, ^{52}Cr, ^{53}Cr
Dwell Time	0.75s
Total Acquisition Time	5 min

3.4 Development of Insoluble Chromium Method

3.4.1 Preliminary Method Development

Method development followed a systematic progression from simple to more complex based on three factors: equipment availability at UNBC, ease of use, and established precedent in similar analytical procedures. Five block digestion methods were trialled on 10 mg of mild steel welding fume reference material (MSWF-1) to access the recovery of iron, manganese and zinc and 10 mg of stainless steel welding fume reference material (SSWF-1). The first trial followed

NIOSH 7303, using 1.25 mL HNO_3 and 1.25 mL HCl for final acid concentrations of 5% each. The second trial was a modification of OSHA ID125G using 2 mL H_2SO_4, 2 mL H_2O_2, and 4 mL HCl, resulting in final concentrations of 4% H_2SO_4 and 8% HCl. Three additional methods were tested: an aqua regia method using 0.75 mL HNO_3 and 2.25 mL HCl (1:3 ratio), a reverse aqua regia using 2.25 mL HNO_3 and 0.75 mL HCl (3:1 ratio). For all block digestion trials, samples were heated to 95˚C over 45 minutes and maintained at 95˚C for 1 hour. After digestion, samples were diluted to 25 mL using DDI water, and calibration standards were matrix-matched to each method's final acid composition.

Based on the recoveries of the SSWF-1 and the chemical nature of spinel chromium compounds, it was determined that more rigorous digestion methods would be required. Typically, this would involve the use of either hydrofluoric acid or perchloric acid; however, these digestion procedures are not feasible at UNBC due to the university's policy of being hydrofluoric acid (HF)-free, implemented to mitigate potential safety and environmental hazards. Alternative approaches using ammonium bifluoride (NH_4HF_2) as an in-situ HF generator were evaluated within UNBC's safety guidelines. Additionally, digestion methods involving perchloric acid were excluded due to the associated safety risks that can arise in the presence of organics. Perchloric acid is a strong mineral acid that may act as an oxidizer and requires specific fume hoods and safety precautions. Additionally, perchloric acid fumes can form explosive metallic perchlorates within the ductwork connected to the fume hood.

The block digestion methods showed incomplete dissolution of the reference materials, particularly for SSWF-1, which contains spinel oxide structures. Based on these results, microwave digestion was explored using an Anton Parr Multiwave 5000 demo unit. Six trials were conducted using various acid combinations to digest 50 mg of Cr_2O_3. In the first trial, 6 mL

HCl, 2 mL HNO_3, and 1 mL 1% NH_4HF_2 were combined to generate HF in situ. Trial 2 used a simplified combination of 5 mL HNO_3 and 1 mL H_2O_2. In trial 3, the nitric acid was increased to 6 mL, while maintaining a constant 1 mL H_2O_2. Trial 4 used the same initial volumes as trial 3 (6 mL HNO_3, 1 mL H_2O_2); however, an additional 1 mL H_2O_2 was added before running a second digestion cycle to enhance oxidation and strengthen digestion. Trials 5 and 6 further increased the oxidizing power by use of 6 mL HNO_3 and 3 mL H_2O_2, with trial 6 including a PVC DIS to evaluate the method's effectiveness on the complete sampling media. The first four trials used a microwave program holding at 400W for 20 minutes, then ramping to 800W over 15 minutes with a 15-minute hold. For trials 5 and 6, the program was modified to hold at 400W for 30 minutes before ramping to 800W over 30 minutes with a 30-minute hold to accommodate the increased H_2O_2 volume and to ensure complete digestion. Temperature and pressure limitations of the system frequently interrupted the power program, particularly when digesting the PVC DIS in trial 6.

Following the acquisition of a MARS6 microwave digestion system, a two-step procedure was developed in consultation with CEM Corporation. Initially, the method used 4.5 mL H_2SO_4, 4 mL HNO_3, and 1.5 mL H_2O_2, followed by an additional 1.5 mL H_2O_2 after the first digestion step. The method performance was evaluated using duplicate samples of PVC DIS with 50 mg Cr_2O_3, 50 mg $NiCr_2O_4$, and a 1:1 mixture of both compounds (25 mg each). Further details of the microwave digestion procedure are described in Section 3.4.2.

After establishing the CEM procedure, NIOSH 7304 was evaluated on the MARS6 system as a potentially refined method alternative. This method uses only concentrated HNO_3 with a maximum temperature of 220°C; however, when testing at concentrations of 0.1, 0.5, and

2 x TLV, recoveries were consistently below 15% for chromium(III) oxide on PVC DIS, with visible solid precipitates remaining after digestion.

UNBC restricts the use of HF or perchloric acid, so the CEM method was selected as an optimal method, as it achieved complete digestion without requiring the use of HF or perchloric acid. While the sulfuric acid in the method can potentially increase wear on the ICP-MS nickel sampler cone, this was deemed acceptable given the robust digestion performance and safety considerations.

3.4.2 Final Insoluble Chromium Digestion Procedure

A method was developed by CEM corporation to digest Cr_2O_3 spiked onto a DIS filter capsule. All sample handling and venting of microwave vessels must be done in a fume hood to prevent exposure to fumes produced. For validation, Cr_2O_3 was used to assess the digestion process. It is expected that the microwave digestion procedure would favour the formation of chromium(III). This method was designed for the CEM MARS6 microwave digestion system with the iPrep 12 (100 mL) vessels. As a safety precaution and to ensure even heating of the samples, only six samples were loaded simultaneously.

The insoluble chromium microwave digestion involved placing the DIS capsule filter side down into the PTFE microwave digestion vessels. The DIS capsule was placed filter-side down to maximize contact with the reagents and to prevent the DIS from floating on top of the solution. To the vessels, 4.5 mL of sulfuric acid and 4 mL of nitric acid were added. Once off-gassing had decreased, 1.5 mL of hydrogen peroxide was added dropwise (1 drop/second). The addition of hydrogen peroxide was vigorous and was done with extreme caution to prevent the contents inside the microwave vessel from shooting out. Samples were allowed to pre-digest for

30 minutes, and microwave vessels were assembled. The pre-digestion step allowed for the DIS capsule to react with the acids at room temperature. The pre-digestion time was selected as 30 minutes because at the end of this time frame, no visible fumes were being produced, and the samples had returned to room temperature, thereby indicating that pre-digestion was complete. Samples were then heated to 220°C for 15 minutes. Once samples had cooled, they were vented, and an additional 1.5 mL of hydrogen peroxide was added. Samples were allowed to digest for 30 minutes and then heated to 280°C for 90 minutes. Samples were cooled to room temperature and then diluted to 50 mL using Type I water. An additional 10-fold dilution was required for a final acid strength of 0.9% sulfuric acid and 0.8% nitric acid for ICP-MS analysis (Table 4). The complete procedure, including specific experimental conditions and EPA 6800 SIDMS correction steps, is detailed in*Figure* A1: Sequential analytical procedure for soluble Cr(VI) and Cr(III) extraction and insoluble Cr microwave digestion

Table 4: ICP-MS conditions used in method validation for insoluble chromium on DIS capsules

Agilent 7500 ICP-MS	
Spray Chamber	Quartz, Scott double-pass
Nebulizer	Ezylok Micromist
Sampler Cone	Agilent Nickel
Skimmer Cone	Agilent Nickel
Acquisition Mode	Spectrum (Multi Tune)
Flow Gas	Plasma 15 L/min
Power RF	1500 W
Reaction Gas	3 mL/min He
Analytical Masses (Dwell Time)	^{52}Cr (0.75 s), ^{55}Mn (0.1 s), ^{57}Fe (0.1 s), ^{60}Ni (0.5 s), ^{66}Zn (0.5 s)
Internal Standards (Dwell Time)	^{7}Li (0.5 s), ^{45}Sc (0.2 s), ^{72}Ge (0.1 s), ^{89}Y (0.1 s), ^{115}In (0.1 s), ^{159}Tb (0.1 s)
Acquisition Time	73.53 s

3.5 Method Validation

3.5.1 Validation Strategy

Method validation for soluble Cr(VI) and Cr(III), and insoluble Cr was adapted from EN ISO 21832[51]. The method validation schemes for soluble Cr and insoluble Cr are illustrated in Figure A2 and Figure A3. Instrumental detection limits were determined by measuring the calibration blank solution ten times. Detection limits were determined using ten blank filters that went through the soluble speciation and insoluble Cr methods. The limit of detection (LOD) and limit of quantification (LOQ) for the soluble Cr species were calculated using the standard deviation of the ten extracted blank filters. The calibration curve was made using liquid calibration standards (method 1) or DIS spiked calibration standards (method 2). Spikes were prepared using NatCr(VI) and NatCr(III) for a calibration standard with concentrations of 0.05, 0.2, 2, 20, 100, and 200 ng/mL for ^{52}Cr(VI) and ^{52}Cr(III). While both methods of calculating detection limits are acceptable, liquid calibration standards require less sample preparation as it does not require the use of a DIS capsule and it does not require the extraction process. Unlike the DIS spiked calibration standards, the liquid calibration standards are not perfectly matrix matched. To compare the effect of chromatographic interferences on the determination of detection limits, both calibration curves were evaluated. It was determined that despite differences in the chromatographic interferences, there was no significant difference between the LOD and LOQ of the two methods. Liquid calibration standards were selected for the detection limits for insoluble Cr due to ease of use and lower cost.

Assessments of measurement variation were completed using DIS capsules that were spiked with varying concentration of ^{Nat}Cr(III), ^{Nat}Cr(VI), ^{50}Cr(III), and ^{53}Cr(VI). The same set of samples were used to determine the measurement variation both with and without the use of the

EPA 6800 isotopic correction calculation. The concentration was determined for data processed without SIDMS using a calibration curve for ^{52}Cr(III) and ^{52}Cr(VI). For data processed using SIDMS, a calibration curve was not required, and data was processed using the calculation provided in EPA 6800. For the soluble extraction, measurement accuracy was evaluated based on the analytical recovery of a minimum of 6 samples at four concentration levels (0.1, 0.5, 1, and 2 x TLV). Concentration levels were determined based on an 8-hour TWA with a sampling flow rate of 2 L/min and are listed in Table 5. Measurement precision was evaluated through analytical repeatability, method repeatability, and intermediate precision. Analytical repeatability was assessed by measuring three samples twice at two different concentration levels (0.1, 0.2, and 1 x TLV). Method repeatability involved analyzing ten samples at five concentration levels (0.1, 0.2, 0.5, 1 and 2 x TLV) and determining the variation between measurements. Intermediate precision was assessed by measuring three samples at three concentration levels (0.1, 0.2, and 1 TLV) at approximately 2- and 24- hours post-extraction to assess variability in the results.

Table 5: Mass loading for Cr(VI) and Cr(III) at different TLV levels based on 8-hour sampling at 2L/min (960 L total air volume).

Level	**^{Nat}Cr(VI)**		**^{Nat}Cr(III)**		**Ratio ^{53}Cr(VI) to ^{52}Cr(VI)**	**Ratio ^{50}Cr(III) to ^{52}Cr(III)**
	Concentration (mg/m^3)	**Mass loading (µg/filter)**	**Concentration (mg/m^3)**	**Mass loading (µg/filter)**		
TLV	0.0002	0.19	0.003	2.9	-	-
0.1 x TLV	0.00002	0.019	0.0003	0.29	1	1
0.2 x TLV	0.00004	0.038	0.0006	0.58	1	1
0.5 x TLV	0.0001	0.096	0.0015	1.4	1	0.1
1 x TLV	0.0002	0.19	0.003	2.9	1	0.1
2 x TLV	0.0004	0.38	0.006	5.8	1	0.1

For the insoluble extraction, a suspension of Cr2O3 analytical repeatability was assessed by collecting six measurements of the same sample at four concentration levels (0.1, 0.5, 1 and 2 x TLV). Method repeatability was determined by measuring ten samples at three concentration levels (0.1, 0.5, 1, and 2 x TLV). Intermediate precision was assessed by measuring three samples at three concentration levels (0.1, 0.5, 1, and 2 x TLV) with at least 24 hours between measurements. Analytical recovery was assessed by digesting ten spiked DIS capsules at three concentration levels (0.1, 0.5, 1, and 2 x TLV). Spikes were prepared using a suspension of 1 mg/L Cr_3O_3 in 10% (v/v) 2-propanol. The suspension was sonicated for 10 minutes, and sonication was continued during the spiking process.

3.5.2 Matrix Effect Studies

Matrix effects were evaluated with a particular focus on the influence of soluble Fe(III), a significant potential interference in workplace air samples. To assess these effects systematically, a series of test samples were prepared at 2 x TLV using various combinations of stainless steel welding fume (SSWF-1), Fe(III) chloride, and chromium species. SSWF-1 was used to simulate real welding fume samples, containing by mass: 30% iron, 23% manganese, 8% chromium, 4% nickel, and <0.5% each of copper and zinc. A 1 mg/mL SSWF-1 suspension was prepared in 10% (v/v) 2-propanol. To ensure uniform particle distribution, the suspension was sonicated for 10 minutes before being pipetted onto DIS capsules. The spiked capsules were dried at 50°C to remove the liquid phase before additional components were added.

Six different sample types were prepared to systematically evaluate potential matrix effects (Table 6). Type I contained only SSWF-1 to establish baseline recovery. Type II combined SSWF-1 with soluble Cr(III) and Cr(VI) to assess the impact of the welding fume matrix on chromium speciation. Type III expanded on the Type II sample by adding isotopic tracers (^{50}Cr(III) and ^{53}Cr(VI)) to evaluate species interconversion. Types IV and V examined the specific effects of soluble iron by using $FeCl_3$ instead of SSWF-1, with Type V including isotopic tracers. Finally, Type VI combined all components - SSWF-1, $FeCl_3$, soluble chromium species, and isotopic tracers - to evaluate potential synergistic effects.

Table 6: Sample types for evaluating matrix effects on the recovery of soluble Cr(III) and Cr(VI), and insoluble Cr

Sample Type	**SSWF-1** 2xTLV 21.0 µg	**$FeCl_3$** - 21.6 µg	**^{Nat}Cr(VI)** 2xTLV	**^{Nat}Cr(III)** 2xTLV	**^{53}Cr(VI)** 2xTLV	**^{50}Cr(III)** 2xTLV
I	•					
II	•		•	•		
III	•		•	•	•	•
IV		•	•	•		
V		•	•	•	•	•
VI	•	•	•	•	•	•

For samples containing multiple components, a consistent addition sequence was followed: first SSWF-1, followed by soluble Cr(III) and Cr(VI) species, then isotopic tracers, and finally soluble iron. All samples then underwent both the soluble and insoluble extraction procedures. This systematic approach allowed for the evaluation of individual and combined matrix effects on method performance, particularly focusing on the impact of soluble Fe(III) on chromium speciation and recovery.

4. Results and Discussion

4.1 Soluble Chromium Analysis

4.1.1 Preliminary Method Development

Initial optimization of the chromatographic separation revealed that using both the AG7 guard column and AS7 analytical column resulted in diminished peak intensity due to the required 10-minute run time. By using only the AG7 guard column, sufficient separation of Cr(III) and Cr(VI) was maintained while reducing the run time to 5 minutes, significantly improving signal intensity.

Investigation of instrument parameters demonstrated that longer dwell times improved the signal-to-noise ratio without compromising chromatographic resolution. Testing of dwell times (0.1, 0.5, 0.6, and 0.75 seconds) showed that 0.75 seconds provided optimal results. Similarly, evaluation of sample loop sizes (50 µL, 250 µL, and 1000 µL) indicated that the 1000 µL loop gave the best sensitivity while maintaining acceptable peak shape.

A significant interference with the Cr(VI) peak was observed during initial method development. To identify the source, systematic testing was performed comparing: uncleaned DIS filters, uncleaned DIS with 5 minutes of airflow (2 L/min), cleaned DIS filters, cleaned DIS with airflow, cleaned filters in water rinsed DIS bodies, and cleaned DIS washed three times with DDI water. There were no notable differences identified between the different filters and washing methods (Figure 2).

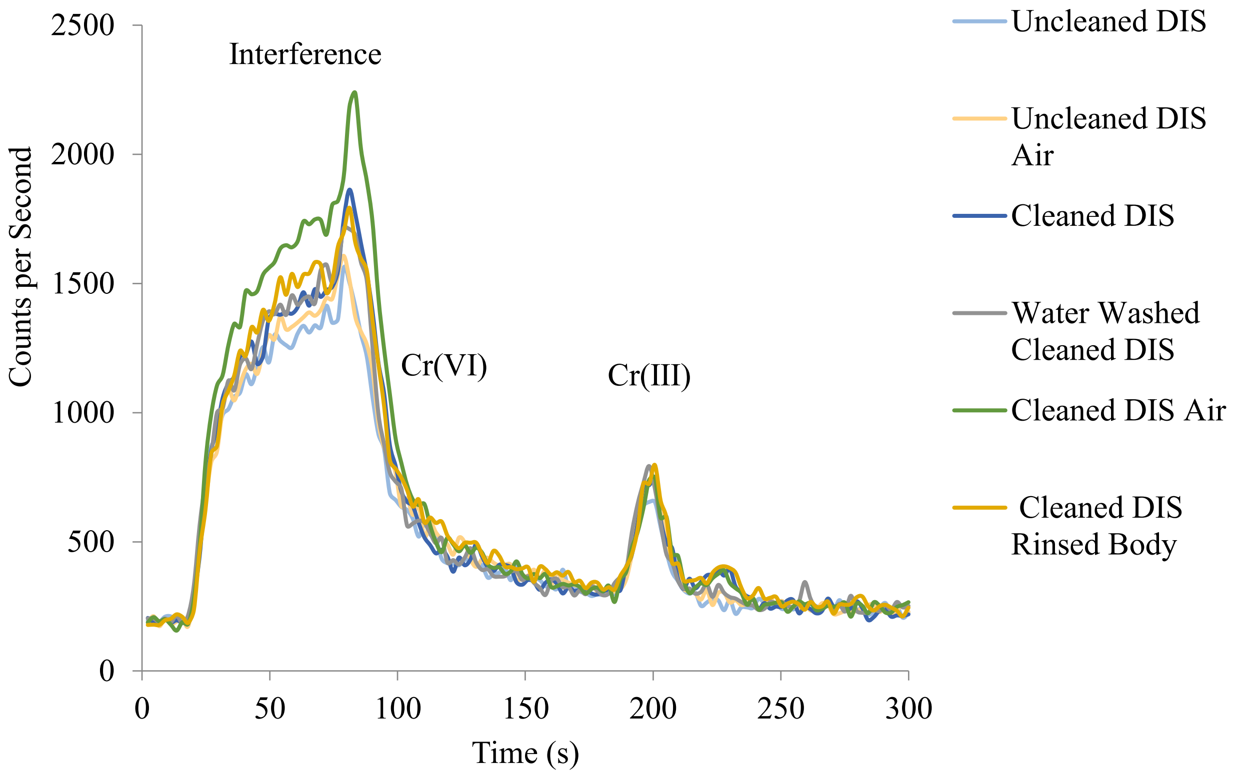


Figure 2: Comparison of uncleaned and cleaned DIS filters with and without air being drawn through.

Testing at flow rates of 0, 1, 2, 3, and 4 mL/min showed that 3 mL/min provided optimal interference reduction while maintaining chromium sensitivity (Figure 3). With optimization in helium collision gas flow, the interference in the region below 100 seconds was successfully reduced. Since this interference was present for m/z 50, 52, and 53 it was thought to be a result of chloride from the PVC filter forming $^{35}\text{Cl}^{15}\text{N}^{+35}$ (m/z 50), $\text{Cl}^{16}\text{O}^{1}\text{H}^{+}$ (m/z 52), and $^{37}\text{Cl}^{16}\text{O}^{+}$ (m/z 53). The helium collision mode effectively minimized polyatomic interferences, particularly the $^{40}\text{Ar}^{12}\text{C}^{+}$ interference that affects ^{52}Cr measurements.

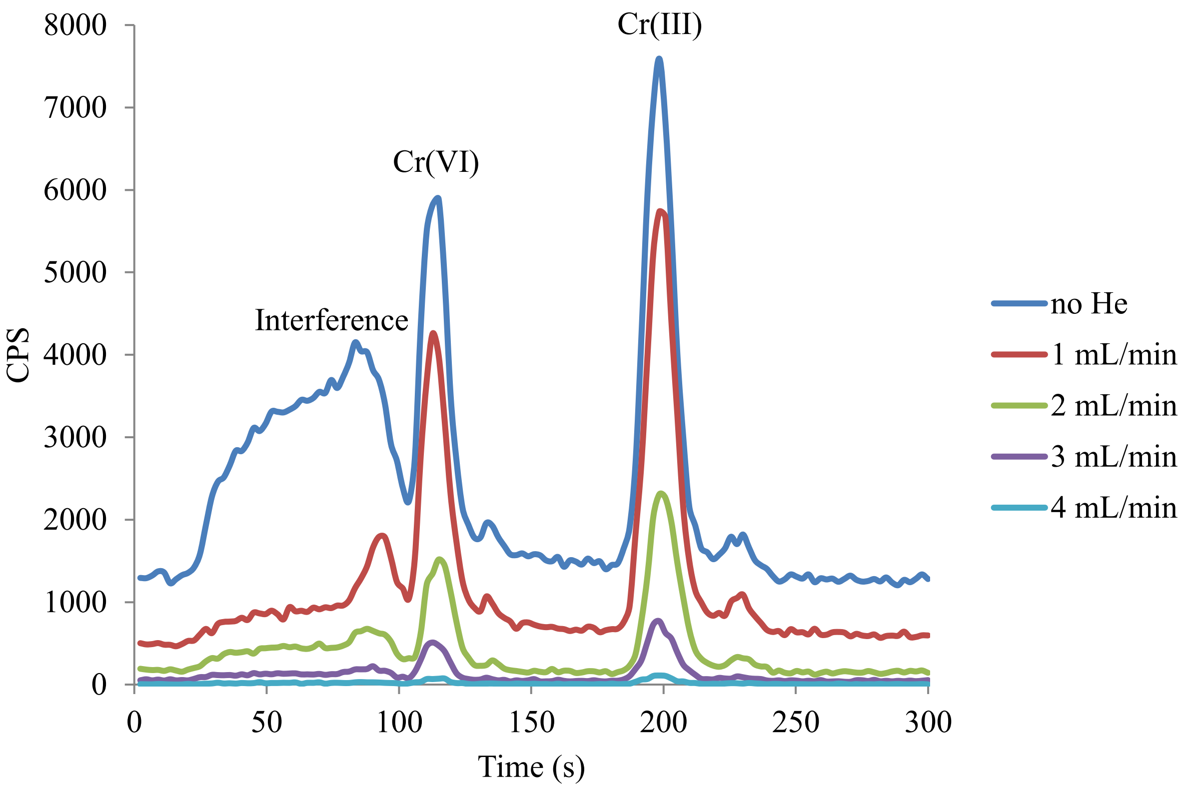


Figure 3: Effect of He collision gas on 50 ng/L Cr(VI) and Cr(III) solution.

The optimization of the helium gas flow resulted in a robust method capable of separating and detecting both chromium species with minimal interference. The final parameters included a 5-minute run time using only the AG7 guard column, 0.75s dwell time, 1000 µL sample loop, and 3 mL/min helium collision gas flow. These conditions provisioned a foundation for subsequent method validation studies.

4.1.2 Detection Limits

Analysis of 10 lab blanks resulted in instrument detection limits (IDL) of less than 0.3 ng/mL (0.1 ng) for Cr(III) and 0.004 ng/mL (0.9 ng) for Cr(VI) (Table 7). LOD and LOQ were determined by two different methods for comparison. For method 1, liquid calibration standards were used. For method 2, spiked DIS samples were used as calibration standards. Due to the increased variability of the interference peak caused by the DIS filters, method 2 is the preferred option because it accounts for the variation in the baseline signal. LODs and LOQs were not significantly different ($t(5) = 1.94$, $p = 0.11$, $\alpha = 0.05$). The LOD for ^{52}Cr(VI) was 0.1 ng for both methods. For Cr(III), LODs ranged from 0.4-2.0 ng depending on the isotope. LOQs for ^{52}Cr(VI) were 0.4 and 0.4 ng for Methods 1 and 2, respectively, while Cr(III) LOQs ranged from 1.1-5.0 ng. In comparison, the estimated LOD for Cr(VI) by NIOSH 7605 is 0.05 µg/sample. For both methods 1 and method 2, the Cr(VI) LOQ was less than 0.03 x TLV for both an 8-hr and 2-hr sampling period (Table 7). The Cr(III) LOQ was less than 0.03 x TLV for an 8-hr, 2-hr, and 15-min sampling period.

Table 7: Instrument detection limits (ng/mL), LOD (ng/filter), and LOQ (ng/filter) for Cr(VI) and Cr(III) isotopes by IC-ICP-MS when liquid calibration standards (method 1) or spiked DIS calibration standards (method 2) were used (n=10)

Detection Limits		**^{50}Cr(VI)**	**^{52}Cr(VI)**	**^{53}Cr(VI)**	**^{50}Cr(III)**	**^{52}Cr(III)**	**^{53}Cr(III)**
IDL (ng/mL)		0.02	0.004	0.01	0.3	0.3	0.3
LOD (ng/filter)	Method 1	0.3	0.1	0.3	1.0	0.4	2
	Method 2	0.5	0.1	0.3	0.9	0.5	2
LOQ (ng/filter)	Method 1	1.1	0.4	1.1	3.2	1.2	5
	Method 2	1.0	0.3	0.9	2.5	1.1	5

4.1.3 Method Performance Without EPA 6800

The precision and accuracy of the soluble Cr(VI) and Cr(III) analysis were assessed across various concentrations, ranging from 0.1, 0.2, 0.5, and 2 times the 8-hour threshold limit value time-weighted average (TLV-TWA) as shown in Table 8. Low-level method repeatability and analytical recovery was assessed at 0.02 x TLV for Cr(VI) and 0.001 x TLV for Cr(III).

Table 8: Precision and accuracy for Cr(VI) and Cr(III) at various concentration levels without the use of EPA 6800 interconversion correction

Cr(VI)	**n**	**0.02 x TLV**	**0.1 x TLV**	**0.2 x TLV**	**0.5 x TLV**	**1 x TLV**	**2 x TLV**
Method Repeatability (%CV)	10	18	12.1	6.46	9.19	25.2	11.3
Intermediate Precision (%CV)	3	-	5.51	8.53	-	12.3	-
Analytical Repeatability (%CV)	3	-	1.15	2.34	-	4.91	-
Analytical Recovery (%)	10	81.0	65.9	81.4	89.3	70.3	85.5
Cr(III)	**n**	**0.001 x TLV**	**0.1 x TLV**	**0.2 x TLV**	**0.5 x TLV**	**1 x TLV**	**2 x TLV**
Method Repeatability (%CV)	10	6.5	8.54	5.95	8.80	2.69	10.7
Intermediate Precision (%CV)	3	-	5.23	5.98	-	60.9	-
Analytical Repeatability (%CV)	3	-	0.93	1.62	-	0.50	-
Analytical Recovery (%)	10	120	68.6	81.8	112	217	103

Without the use of isotopic correction by EPA Method 6800, the method exhibited varying levels of precision and accuracy (Table 8). For Cr(VI), method repeatability ranged from 6.46 % to 25.2 %, with the highest variability at 1 x TLV. Intermediated precision for Cr(VI) ranged from 5.51 to 12.3 %, while analytical repeatability remained below 5 % for all tested concentration levels. The recoveries for Cr(VI) ranged from 65.9% to 89.3 %, with the lowest recovery at 0.1 x TLV.

For Cr(III), the method repeatability was more consistent, with CV ranging from 2.69 % to 10.7 %. However, the intermediated precision showed substantial variability, particularly at the 1 x TLV, where the CV reached 60.9%. Analytical repeatability remained below 2 % across all concentrations. The most concerning finding was the wide range of analytical recoveries for

Cr(III), spanning from 68.6 % to 217 %, with the highest recovery observed at 1 x TLV. These results indicate that while some aspects of the method meet the conventional acceptance criteria for NIOSH and OSHA (CVs below 20 % and recoveries between 75 to 125 %), several parameters exceed these limits. While ISO requires an analytical recovery ranging from 90 to 110 %, this strict criteria is often difficult to achieve with real workplace samples due to complex matrices and varying environmental conditions. The broader NIOSH and OSHA range better reflects the practical challenges encountered in field sample analysis.

The Cr(III) recovery at 1 x TLV (217 %) with corresponding high intermediate prevision (60.9 %) are unsatisfactory and indicate methodological issue requiring further investigation. Further examination of the intermediate precision revealed significant day-to-day variation that had not been seen at the other TLV levels for Cr(III) or Cr(VI). Notably, the recovery of the 1 x TLV Cr(III) sample was 217% on day 1, however when the same samples were run on day 2 the recoveries were 99.4%. Meanwhile, the recoveries for Cr(VI) only varied from 70.3 % (day 1) to 70.2 % (day 2). This suggests that there was a random error in the measurement of Cr(III) at 1 x TLV. If the high Cr(III) recovery on day 1 was attributed to interconversion of Cr(III) to Cr(VI), a change in the Cr(VI) recovery between day 1 and day 2 would have been expected.

These inconsistencies could be re-evaluated using a new set spiked samples at 1 x TLV to determine if the cause was random error, bias in the calibration curve for Cr(III), or sample instability. Method performance could potentially be improved by using a pH 8 buffer as described in ASTM D6832 or by implementing an internal standard correction, provided the ICP-MS software allows internal standard correction in time-resolved analysis mode[29,30]. The primary objective of this portion of the research was to assess method performance and species interconversion in the absence of EPA 6800 SIDMS techniques, thereby establishing a baseline for the potential benefits of isotopic tracking and correction; therefore, further optimization of the non-isotopic method, though technically feasible, would not serve the comparative purpose of this investigation.

4.1.4 Method Performance with EPA 6800

The use of EPA 6800 improved the precision and accuracy of the soluble extraction when compared to the results without the use of isotopic spikes. The use of EPA 6800 resulted in the method repeatability, intermediate precision, and analytical repeatability being less than 5 % (Table 9). The most notable difference was a decrease in the method repeatability of Cr(VI) at 0.1 x TLV from 12 % to 2.3 % when applying EPA 6800. Using the EPA 6800 method, any interconversion that occurred between the initial time the sample was run and 24 hours later was corrected, as evidenced by, the low intermediate precision. Cr(VI) recoveries ranged from 99 % to 109 % when tested at 0.1, 0.2, 0.5, and 2 x TLV. The analytical recovery for Cr(III) was 95 % at 0.1 and 0.2 x TLV; however, it increased to 175 % at 0.5 x TLV, 167 % at 1 x TLV and 172 % at 2 x TLV. This is indicative of a positive bias above 0.5 x TLV. Further work is required to determine if this bias can be improved or eliminated. Additionally, EPA 6800 defines an acceptable ratio of 1:10 or 0.1 to 1 for isotopic spike to the expected concentration. To conserve isotopic spikes, the ratio was set to 0.1 for $^{50/52}$Cr(III) for the 0.5, 1, and 2 x TLV tests. Further testing is required to verify if the isotopic ratio is the cause of the overestimation of Cr(III) at 0.5, 1, and 2 x the TLV.

Table 9: Precision and accuracy for Cr(VI) and Cr(III) at various concentration levels using EPA 6800 interconversion correction.

Cr(VI)	**n**	**0.1 x TLV**	**0.2 x TLV**	**0.5 x TLV**	**1 x TLV**	**2 x TLV**
Method Repeatability (%CV)	10	2.3	2.1	2.2	4.0	1.1
Intermediate Precision (%CV)	3	1.69	2.4	-	2.7	-
Analytical Repeatability (%CV)	3	2.0	1.9	-	1.8	-
Analytical Recovery (%)	10	99	100	107	109	108
Cr(III)	**n**	**0.1 x TLV**	**0.2 x TLV**	**0.5 x TLV**	**1 x TLV**	**2 x TLV**
Method Repeatability (%CV)	c	0.43	1.7	2.0	0.87	0.76
Intermediate Precision (%CV)	3	0.85	2.5	-	0.52	-
Analytical Repeatability (%CV)	3	0.81	0.16	-	1.6	-
Analytical Recovery (%)	10	95	95	175	167	172

4.2 Insoluble Chromium Analysis

4.2.1 Preliminary Method Development

Initial evaluation of hot block digestion methods revealed varying effectiveness for different sample types. As shown in Figure 5, recoveries from mild steel welding fumes (MSWF-1) ranged from 68 to 114 % for iron, with NIOSH 7303 achieving 97.5 % recovery. When this method was applied to stainless steel welding fumes (SSWF-1) (Figure 5), recoveries were significantly lower, indicating these methods were insufficient for more complex spinel oxide structures.

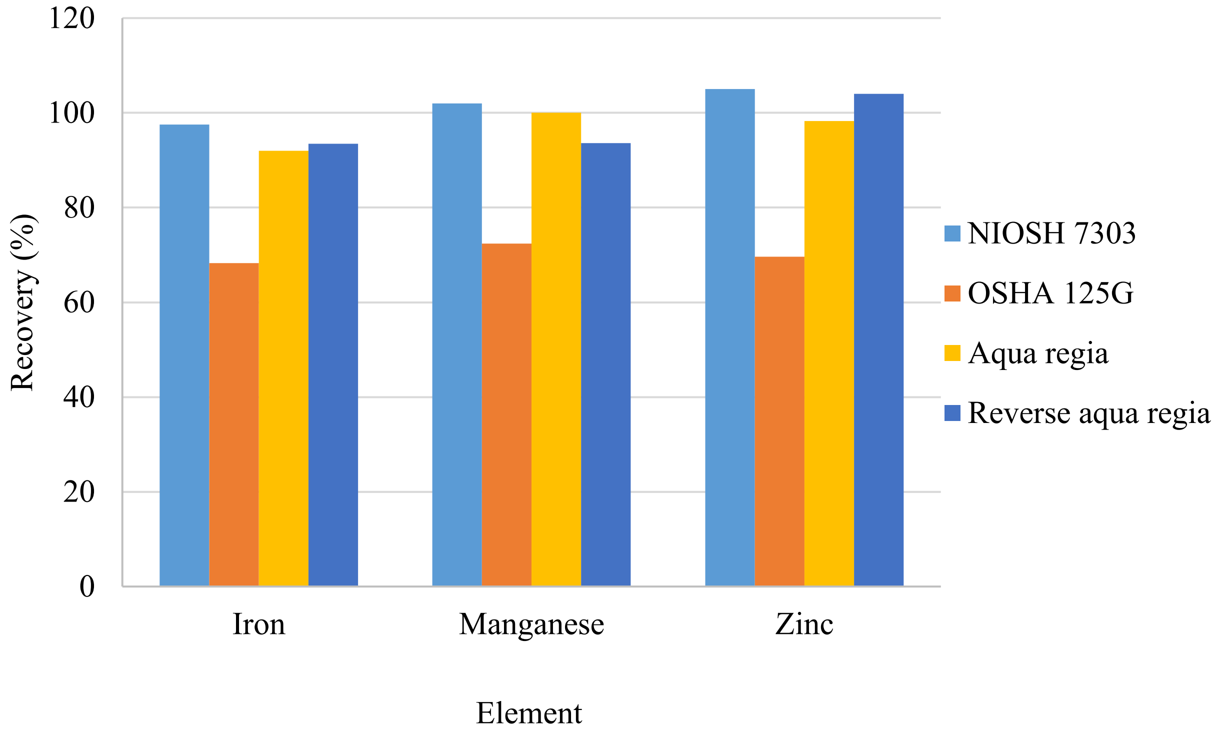


Figure 4: Recovery of mild steel welding fumes (MSWF-1) by block digestion methods

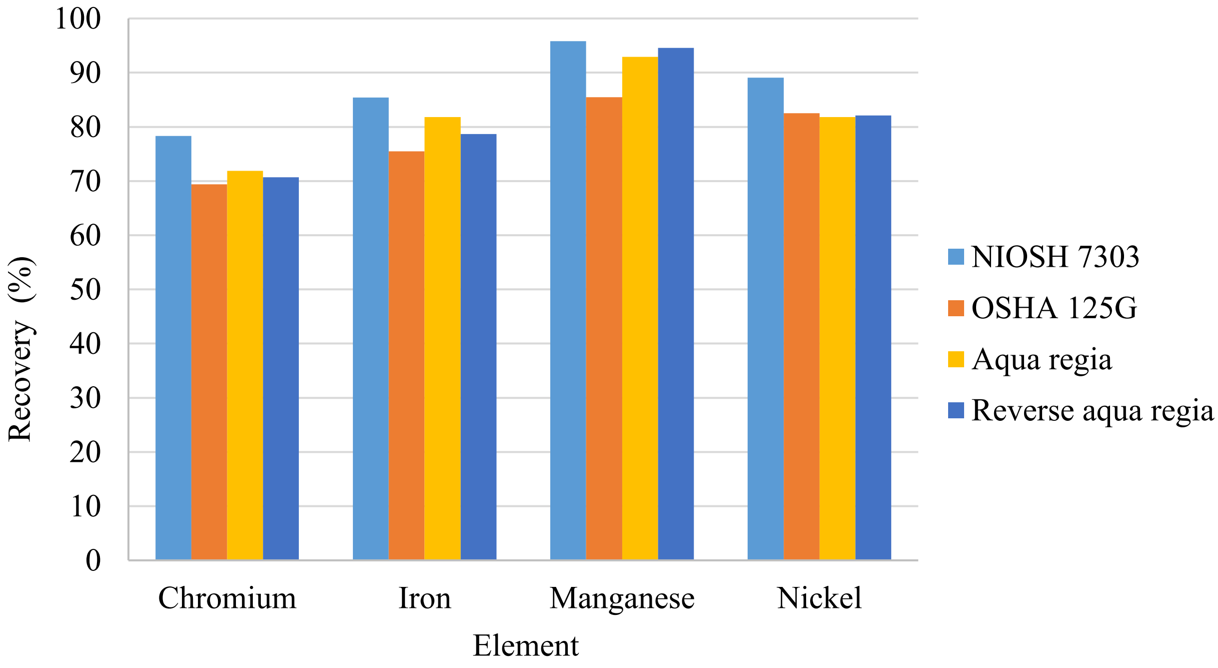


Figure 5: Summary of the recovery for stainless steel welding fumes (SSWF-1) by block digestion methods

The Anton Parr microwave digestion trials evaluated different acid combinations and digestion parameters using spikes of approximately 50 mg Cr_2O_3 (34.2 mg Cr). Initial attempts using $HCl/HNO_3/NH_4HF_2$ (Trial 1) yielded only 0.3% recovery, with significant solid residue remaining (Figure 6). This was unexpected as ammonium bifluoride normally improves the digestion of Cr_2O_3. It is possible that using a smaller volume of more concentrated NH_4HF_2 would improve the recovery. The nitric acid and hydrogen peroxide combinations in Trials 2-4 significantly improved recoveries (87.5-94.2 %), though small amounts of green Cr_2O_3 particulates remained visible in the purple solutions. The highest recovery of 94.2% was achieved in Trial 4 using 6 mL HNO_3 with two separate 1 mL additions of H_2O_2. In trial 5, the procedure was further modified using 6 mL HNO_3 and 3 mL H_2O_2, achieving 89.7 % recovery with no visible particulates and a blue solution colour. When these optimized conditions were applied to a sample containing PVC filter material in Trial 6, the recovery decreased to 79.3 %, suggesting some matrix effects from the filter material. Based on these results and UNBC safety requirements prohibiting the use of hydrofluoric and perchloric acids, further method development was pursued using a CEM MARS6 microwave system. The Anton Parr microwave digestion trials showed progressive improvement with the modification of acid mixtures and digestion parameters. Another limitation observed during these trials is that the microwave runs did not run to completion due to a maximum pressure error unless the vessels were vented mid-way through the run.

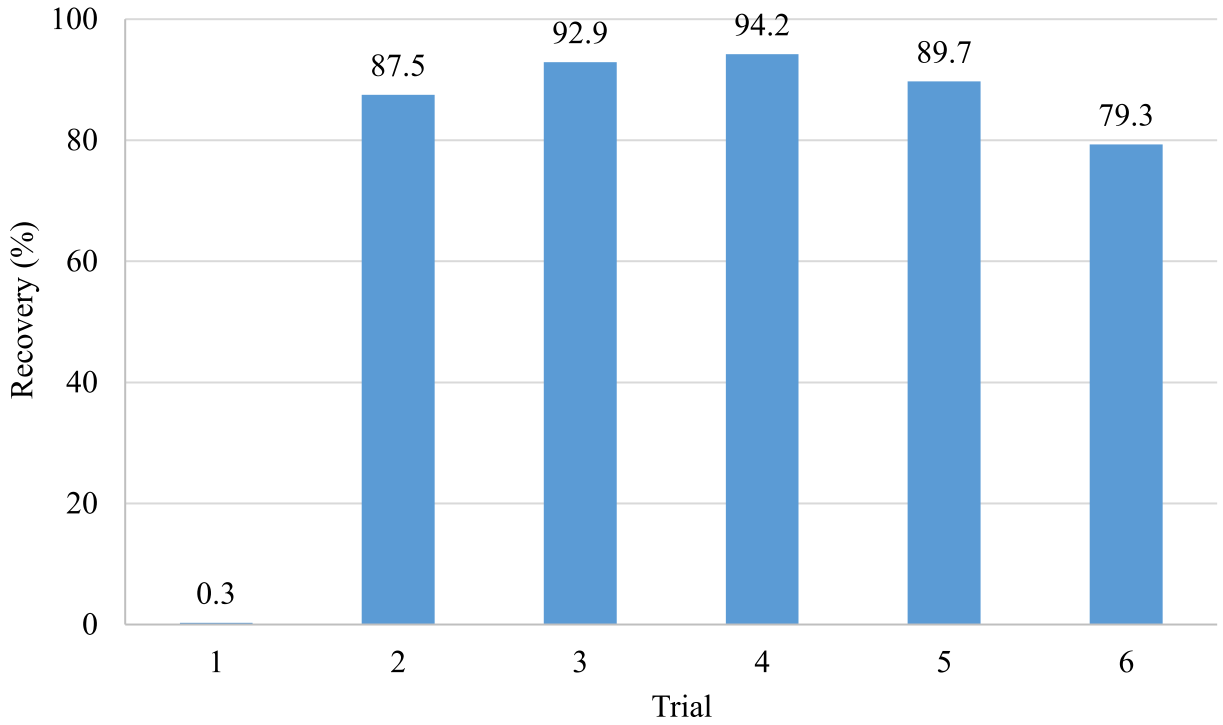


Figure 6: Recovery of 50 mg of Cr_2O_3 by Anton Parr Microwave Digestion Methods

The CEM microwave digestion method demonstrated superior performance. As shown in Figure 7, the two-step procedure using HNO_3, H_2SO_4, and H_2O_2 achieved 96 % recovery for both chromium and nickel from Cr_2O_3 and $NiCr_2O_4$ samples. This method successfully dissolved the spinel oxide structures while accommodating the PVC filter material. The stepwise addition of H_2O_2 proved crucial for managing the vigorous reaction with the PVC filter while maintaining digestion efficiency.

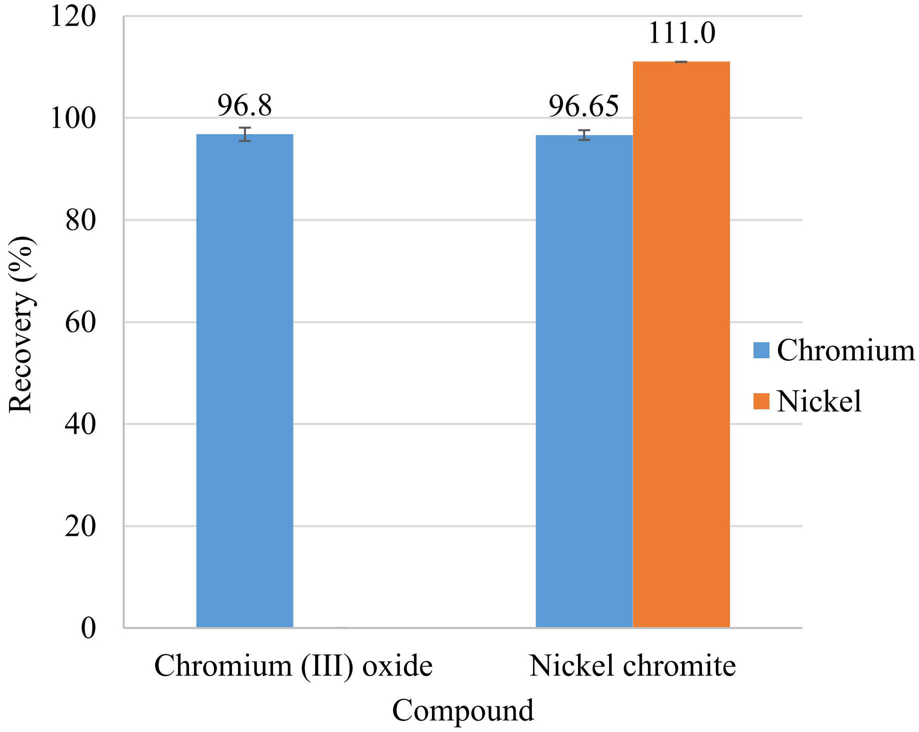


Figure 7: Recoveries of Chromium and Nickel by CEM Microwave Digestion Method using HNO_3, H_2SO_4, and H_2O_2

Subsequent testing of NIOSH 7304 using 10 mL of HNO_3 on the MARS6 system (Figure 8) demonstrated consistent poor performance, with recoveries below 15 % across all concentration levels (0.1, 0.5, and 2 x TLV). At the maximum temperature of 220°C, the nitric acid-only digestion was insufficient for breaking down the spinel oxide structures, leaving visible precipitates in the digestion vessels.

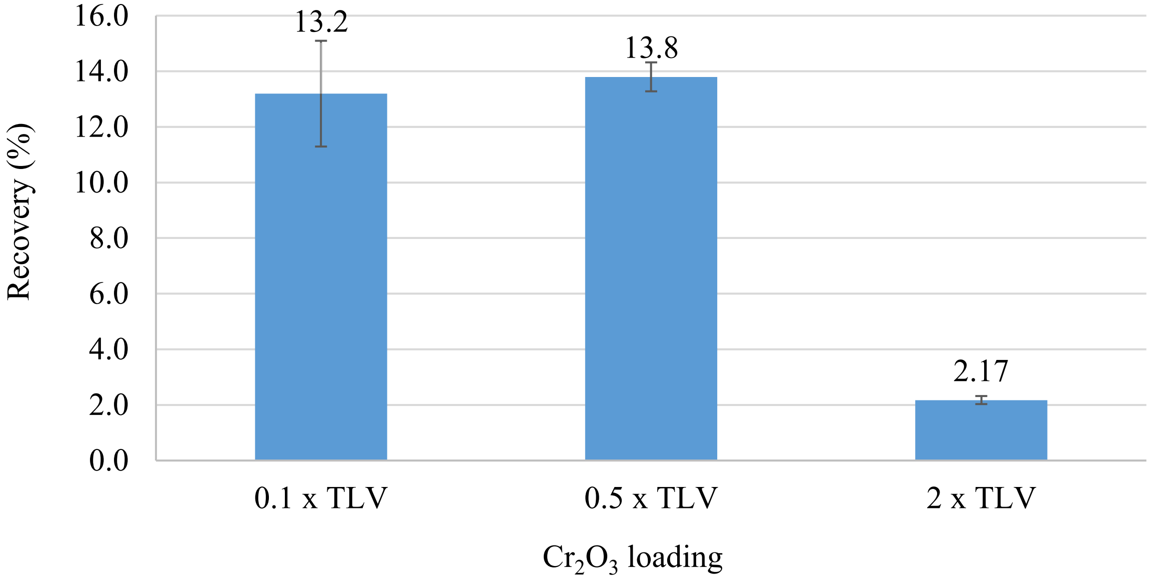


Figure 8: Recovery of chromium from Cr_2O_3 at 0.1, 0.5, and 2 x TLV by NIOSH 7304

When integrating these findings with the soluble extraction procedure, the CEM method maintained robust performance but showed slightly reduced recoveries compared to standalone digestion. This indicated potential losses during the sequential extraction process that required further investigation in the method validation phase.

4.2.1 Detection Limits

The insoluble chromium detection limits were evaluated as both an individual method and as part of the sequential method following the soluble extraction (Table 10). LOQs were similar for the individual and sequential methods, with only minor variations in the IDL and LOD.

This suggests that there was minimal chromium contamination when performing soluble extraction followed by the insoluble extraction. LOQs for insoluble chromium were less than 0.03 x 8-hr TLV as required by EN ISO 21832[51]. In comparison, the estimated LOQ by OSHA ID-125G is 1.3 µg.

Table 10: Instrument detection limit (µg/L) , limit of detection (µg/filter) , and limit of quantification (µg/filter) for insoluble chromium extraction: standalone and sequential extraction after soluble extraction (n=10)

	Insoluble Only	**Insoluble digest after soluble extraction**
IDL (µg/L)	0.2	0.2
LOD (µg/filter)	0.3	0.4
LOQ (µg/filter)	0.9	0.9

4.2.2 Method Performance

The precision and accuracy of the standalone insoluble digestion was evaluated using a series of DIS filters spiked at 0.1, 0.5, 1, and 2 x TLV using either a 0.1 mg/mL or 1 mg/mL chromium(III) oxide suspension (Table 11). Method repeatability, intermediate precision, and analytical repeatability were below 20% for all spike levels. The analytical recovery ranged from 90.2 to 105 % over the spike levels. Increased method variability and intermediate precision can arise from the filter spiking process and the particle size variability in the suspension. Due to the nature of the Cr_2O_3 suspension used, it is possible for small particulates to cluster together through flocculation. This results in variability in the amount of Cr_2O_3 particles transferred onto the DIS capsule. This error was minimized by sonicating the solution to break up clusters of particulates and pipetting the solution while the ultrasonic bath was running.

Table 11: Precision and accuracy of the standalone insoluble chromium extraction

	n	0.1 x TLV	0.5 x TLV	1 x TLV	2 x TLV
Method Repeatability (% CV)	10	13.6	5.39	7.85	8.01
Intermediate Precision (% CV)	3	15.2	4.63	4.85	2.45
Analytical Repeatability (% CV)	6	4.5	2.1	1.92	1.04
Analytical Recovery (%)	10	105	93.5	90.2	97.5

4.3 Matrix Effects and Method Limitations

The matrix effects studies revealed complex interactions between welding fumes, soluble iron, and chromium species that significantly impacted method performance. The evaluation used six different sample types at 2 x TLV to systematically assess these effects (Table 12).

Table 12: Effect of stainless steel welding fumes and soluble Fe(III) on the recoveries of soluble Cr(VI) and Cr(III) and insoluble chromium without using EPA 6800 (n=3)

Sample Type	Composition	Recovery (%)		
		Cr(VI)	Cr(III)	Insoluble Cr
I	SSWF-1 only	-	-	78
II	SSWF-1 + Natural Cr	104	92	80
III	SSWF-1 + Natural Cr + Isotopes	126	99	80
IV	$FeCl_3$ + Natural Cr	52	105	-
V	$FeCl_3$ + Natural Cr + Isotopes	64	100	-
VI	All components	102	106	75

Initial testing with SSWF-1 alone (Type I) achieved 78 % recovery of insoluble chromium, establishing a baseline for the welding fume matrix. When soluble Cr(III) and Cr(VI) were added to SSWF-1 (Type II), recoveries improved to 92 % for Cr(III) and 10 4% for Cr(VI). This suggests the presence of soluble chromium species does not negatively impact recovery from the welding fume matrix, an observation that aligns with findings previously reported by Ashley et al. (2009) in their evaluation of sequential extraction procedures for Cr(VI)[30].

The most significant matrix effect was observed with soluble Fe(III). In samples containing only $FeCl_3$ (Types IV and V), Cr(VI) recoveries dropped dramatically to 52-64 %, likely due to the formation of iron chromate complexes ($FeOHCrO_4 \cdot 2Fe(OH)_3$) or through the direct reduction Cr^{6+} to form Fe^{2+} and Cr^{3+} (Figure 9). Interestingly, Cr(III) recoveries remained robust at 100 to 105 %, indicating the interference specifically affects hexavalent chromium. However, when both SSWF-1 and $FeCl_3$ were present (Type VI), Cr(VI) recovery improved to 102 %, suggesting components in the welding fume matrix may help stabilize Cr(VI) against Fe(III) interference. This could occur through surface passivation as oxide layers on SSWF-1 particles may absorb or react with the Fe(III), thereby minimizing the amount of free Fe(III) available for the reduction of Cr(VI). This reduction in recoveries was also observed by Ashley et al. when they exposed 10 µg of soluble potassium chromate to 250 µg of iron (II) sulfate[30]. When water was used as the extraction solution, the recoveries ranged from 24-32 %[30]. In comparison, the recoveries were 66-88 % when ammonium sulfate/ammonium hydroxide was used as the extraction solution[30].

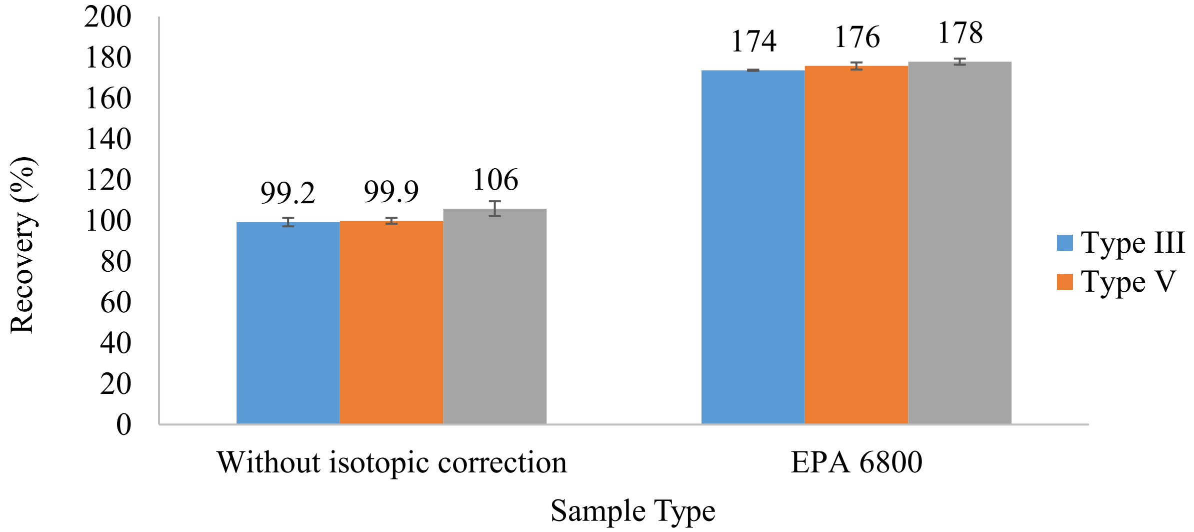


Figure 9: Effect of stainless steel welding fumes and soluble Fe(III) on the recoveries of soluble Cr(III) compared without and with isotopic correction using EPA 6800

The application of EPA 6800 SIDMS to samples III, V, and VI revealed an average Cr(VI) to Cr(III) interconversion rate of 18 %. This interconversion could be successfully corrected using the isotope dilution technique. However, at 2 x TLV, Cr(III) recoveries were consistently higher (approximately 176 %), suggesting potential detector saturation issues at higher concentrations (Figure 10).

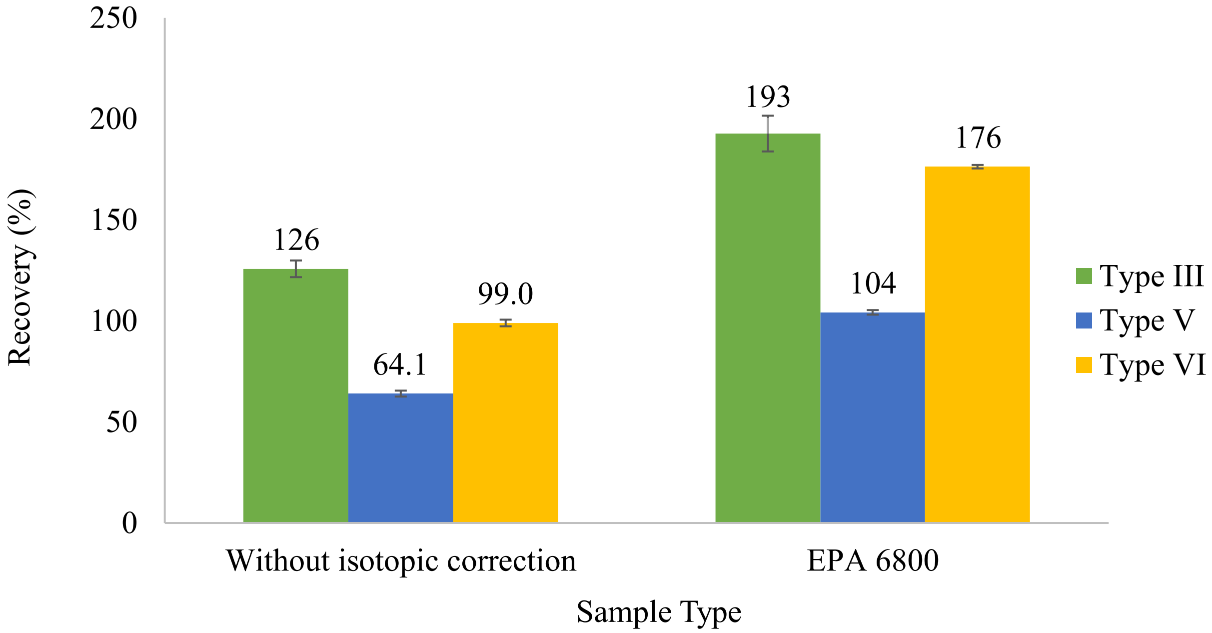


Figure 10: Effect of stainless steel welding fumes and soluble Fe(III) on the recoveries of soluble Cr(VI) compared without and with isotopic correction using EPA 6800

The sequential extraction procedure showed consistently lower recoveries (75-80 %) for insoluble chromium compared to the 97.5 % achieved during standalone method validation. This reduction in recovery is likely due to the loss of fine SSWF-1 particulates during the vacuum filtration and rinsing steps, as particles smaller than the 5-micron PVC filter pore size may pass through during the soluble extraction phase.

Method precision remained robust despite these matrix effects, with coefficients of variation less than 8 % for soluble Cr(VI) and Cr(III), and less than 5% for insoluble chromium across all sample types. These results suggest that while matrix effects can impact absolute recovery, the method maintains good precision and reproducibility.

Further investigation is needed to fully characterize the matrix effects, particularly at lower concentration levels (0.1 and 0.5 x TLV). Additionally, expanding the scope and examining the effects of other metallic oxidizers, such as iron(II), manganese, and aluminum, would be of interest. Additionally, the high Cr(III) recoveries observed at 2 x TLV warrant further study to optimize detector response and potentially adjust isotopic spike ratios for improved accuracy at higher concentration ranges.

4.4 Implications for Further Research

The results of the initial method validation demonstrate promising recoveries for both soluble and insoluble fractions; however, the sequential process reveals a lower soluble Cr(VI) recovery of 75 to80 % (Figure 9), indicating potential loss of fine insoluble chromium particulates during the filtration step. This loss is likely due to fine particulates passing through the DIS 5-micron PVC filter during the soluble filtration. This limitation needs to be examined further before the sequential process of soluble Cr speciation and insoluble Cr method can be implemented.

These findings from this study illustrate the need for further testing to verify method recoveries, specifically for stainless steel welding fumes. Based on the approaches of Ashley et al. (2009) and Tirez et al. (2011), further investigation should focus on evaluating a pH 8 ammonium sulfate/ammonium hydroxide buffer as an alternative to current acidic conditions, evaluation of Fe(II), Fe(III), and Mn matrix effect on species recovery and stability[30,44]. Additionally, it is crucial to establish the linearity of the method and the method's detection limit from sampling to detection. This can be achieved by spiking filters with soluble Cr(III) and Cr(VI) and collecting samples at welding shops. To complete the field validation, a minimum of 3 samples per day should be collected to verify that the recoveries are greater than 75 %, per NIOSH and OSHA standards. To further validate, the collected data, including Cr(III), Cr(VI), and total chromium levels obtained from the various sites, would provide the standard deviations from replicate samples. To enhance the reliability of the findings, blind samples could be incorporated, facilitating a comprehensive post-analysis statistical comparison.

To validate and document the proposed method, it is essential to recognize that the successful completion of this phase hinges upon securing sufficient financial resources. This will further ensure the credibility and integrity of the research. A round robin could be conducted to strengthen its validity, enabling an inter-laboratory comparison of the proposed method. Samples could be collected in a welding shop in Prince George and sent to at least six laboratories within North America and Europe for analysis.

The results of this report are intended to be published in an academic peer-reviewed journal to widely disseminate the validated procedure and its findings. This research was presented at the November 2023 AIHA Sampling and Laboratory Analysis Committee meeting. Furthermore, there is a strong aspiration to elevate the proposed method to the status of a recognized Standard through the American Society for Testing and Materials (ASTM International). This would reinforce the significance of the research within the scientific community and ensure its broader adoption and integration into industrial practices.

5. Conclusion

This research project has successfully developed a method for the quantification of soluble Cr(III) and Cr(VI) as well as insoluble Cr on Disposable Inhalable Samplers (DIS). The method's application can be optimized based on the expected sample matrix, as documented in previous studies by Ashley et. Al (2009)[30]. For example, chrome plating operation primarily generates soluble Cr(VI) compounds, while refractory materials processing typically produces insoluble chromium species[30]. Welding operation, particularly on stainless steel, can generate both soluble and insoluble chromium compounds, necessitating the full sequential procedure[30].

The method developed utilizing EPA Method 6800 Elemental and Molecular Speciated Isotope Dilution Mass Spectrometry enables precise quantification of Cr(VI) and Cr(III) speciation at 0.1 x TLV. Additionally, a digestion procedure designed explicitly for insoluble chromium ensures complete dissolution of chromium compounds with spinel oxide structures without the use of hydrofluoric acid or perchloric acid. Limits of quantification were determined to be less than 0.03 x 8-hr TLV. Analytical precision and accuracy for the method were within the desired range of less than 20 %.

The method validation demonstrated that using EPA 6800 SIDMS significantly improved precision, achieving 99 to 109 % recoveries for Cr(VI) at concentrations from 0.1 to 2 x TLV. The standalone insoluble chromium digestion achieved robust recoveries between 90-105 %, making it particularly suitable for samples known to contain primarily insoluble species. However, the sequential procedure resulted in lower recoveries of 75-80 %, indicating potential losses during filtration. This limitation must be addressed before the sequential method can be widely implemented, particularly for complex matrices like welding fumes, where both soluble and insoluble species are expected.

Matrix effect studies revealed that soluble Fe(III) reduced Cr(VI) recoveries to 52-64 %. This interference could be corrected using isotope dilution techniques. On average, 18 % Cr(VI) to Cr(III) interconversion was observed and successfully corrected using SIDMS. These findings emphasize the importance of controlling extraction conditions and highlight the value of using isotope dilution for accurate speciation results.

The complete analytical workflow, detailed in Figure A1 of the Appendix, illustrates the interconnection between soluble extraction, EPA 6800 SIDMS correction, and insoluble chromium analysis. The flowchart includes decision points for laboratories to either perform the complete sequential procedure or proceed directly with total chromium analysis through the insoluble digestion procedure alone based on knowledge of the expected matrix. When following the complete sequential procedure, soluble Cr(III) and Cr(VI) are first extracted and analyzed followed by insoluble chromium determination, on the same filter. Alternatively, proceeding directly to insoluble digestion yields total chromium. Figure A1 includes all critical experimental parameters, providing analytical laboratories with the detailed information needed to implement either the sequential or separate analytical methods based on matrix composition.

As exposure limits for airborne Cr(VI) tighten, precise analytical methods are essential for both compliance and worker safety. This study provides a sensitive approach for chromium speciation, detecting trace levels well below current limits. By distinguishing between soluble and insoluble forms and addressing interferences, it enhances exposure assessments in high-risk industries. This capability enables industrial hygiene programs to adapt to evolving regulations while strengthening workplace health and safety.

References

(1) DesMarias, T. L.; Costa, M. Mechanisms of Chromium-Induced Toxicity. *Current Opinion in Toxicology* **2019**, *14*, 1–7. https://doi.org/10.1016/j.cotox.2019.05.003.

(2) Jobby, R.; Jha, P.; Yadav, A. K.; Desai, N. Biosorption and Biotransformation of Hexavalent Chromium [Cr(VI)]: A Comprehensive Review. *Chemosphere* **2018**, *207*, 255–266. https://doi.org/10.1016/j.chemosphere.2018.05.050.

(3) Costa, M. Toxicity and Carcinogenicity of Cr(VI) in Animal Models and Humans. *Critical Reviews in Toxicology* **1997**, *27* (5), 431–442. https://doi.org/10.3109/10408449709078442.

(4) NIOSH. *Criteria for a Recommended Standard: Occupational Exposure to Hexavalent Chromium*; Department of Health and Human Services Publication 2013–128; National Institute for Occupational Safety and Health, 2013.

(5) OSHA. *Occupational Exposure to Hexavalent Chromium*; Federal Register 71(39); Occupational Safety and Health Administration, 2006; pp 10099–10385.

(6) IARC. *Chromium (VI) Compounds*; IARC Monographs on the Evaluation of Carcinogenic Risks to Humans; International Agency for Research on Cancer: Lyon, France, 2012; Vol. 100C.

(7) Ashley, K.; Sammarco, J. Factors Affecting Exposure to Hexavalent Chromium in the Workplace. *Journal of Occupational and Environmental Hygiene* **2021**, *18* (4), 142–158.

(8) Park, R. M.; Bena, J. F.; Stayner, L. T.; Smith, R. J.; Gibb, H. J.; Lees, P. S. Hexavalent Chromium and Lung Cancer in the Chromate Industry: A Quantitative Risk Assessment. *Risk Analysis* **2004**, *24* (5), 1099–1108.

(9) Swaroop, A.; Bagchi, M.; Preuss, H. G.; Zafra-Stone, S.; Ahmad, T.; Bagchi, D. Benefits of Chromium(III) Complexes in Animal and Human Health. In *The Nutritional Biochemistry of Chromium (III)*; Elsevier, 2019; pp 251–278. https://doi.org/10.1016/B978-0-444-64121-2.00008-8.

(10) United States Department of Labor, Occupational Safety and Health Administration. Chromium, 2020. https://www.osha.gov/SLTC/chromium/index.html.

(11) ACGIH. *TLVs® and BEIs® Based on the Documentation of the Threshold Limit Values for Chemical Substances and Physical Agents and Biological Exposure Indices*; ACGIH Publications: Cincinnati, 2024.

(12) CAREX Canada. *Chromium (Hexavalent) - Occupational Exposures*; CAREX Canada, 2019. https://www.carexcanada.ca/profile/chromium_hexavalent-occupational-exposures/.

(13) Government of British Columbia. Employment by Industry and Occupation for BC, 2024. https://catalogue.data.gov.bc.ca/dataset/labour-market-outlook/resource/22fbd2a4-ab98-45e1-bdd9-cb4a0aebfb5b.

(14) NIOSH. *NIOSH 7605: Chromium, Hexavalent by Ion Chromatography*; Manual of Analytical Methods NMAM Fifth Edition; National Institute for Occupational Safety and Health, 1994. https://www.cdc.gov/niosh/docs/2003-154/pdfs/7605.pdf.

(15) NIOSH. *NIOSH 7600: Chromium, Hexavalent*; Manual of Analytical Methods NMAM Fourth Edition; National Institute for Occupational Safety and Health, 1994. https://www.cdc.gov/niosh/docs/2003-154/pdfs/7600.pdf.

(16) NIOSH. *NIOSH 7703: Chromium, Hexavalent, by Field-Portable Spectrophotometry*; Manual of Analytical Methods NMAM Fourth Edition; National Institute for Occupational Safety and Health, 2003. https://www.cdc.gov/niosh/docs/2003-154/pdfs/7703.pdf.

(17) NIOSH. *NIOSH 7604: Chromium, Hexavalent*; Manual of Analytical Methods NMAM Fifth Edition; National Institute for Occupational Safety and Health, 1994. https://www.cdc.gov/niosh/docs/2003-154/pdfs/7604-HISTORICAL.pdf.

(18) WorkSafe BC. *Chromium Substances: 2018 ACGIH TLVs for Chromium Substance*; Technical Report; WorkSafe BC, 2020.

(19) ISO. *Air Quality - Particle Size Fraction Definitions for Health-Related Sampling*; Standard 7708:1995; International Organization for Standardization: Geneva, Switzerland, 1995.

(20) Inhalable Sampler Disposable PVC/PVC - 10/Box. https://www.zefon.com/sampler-inhalable-disp-pvcpvc-10bx.

(21) Rubenstein, M. Hexavalent Chromium and Total Chromium Removal from Polychlorinated Vinyl Chloride (PVC) Polymers, 2011.

(22) Xing, L.; Beauchemin, D. Chromium Speciation at Trace Level in Potable Water Using Hyphenated Ion Exchange Chromatography and Inductively Coupled Plasma Mass Spectrometry with Collision/Reaction Interface. *Journal of Analytical Atomic Spectrometry* **2010**, *25* (7), 1046–1055. https://doi.org/10.1039/C004699J.

(23) Meng, Q.; Fan, Z.; Buckley, B.; Lin, L.; Huang, L.; Yu, C.; Stiles, R.; Bonanno, L. Development and Evaluation of a Method for Hexavalent Chromium in Ambient Air Using IC-ICPMS. *Atmospheric Environment* **2011**, *45* (11), 2021–2027. https://doi.org/10.1016/j.atmosenv.2011.02.009.

(24) Zatka, V. J. Speciation of Hexavalent Chromium in Welding Fumes Interference by Air Oxidation of Chromium. *American Industrial Hygiene Association Journal* **1985**, *46* (6), 327–331. https://doi.org/10.1080/15298668591394914.

(25) Ashley, K.; Howe, A. M.; Demange, M.; Nygren, O. Sampling and Analysis Considerations for the Determination of Hexavalent Chromium in Workplace Air. *Journal of Environmental Monitoring* **2003**, *5*, 707–716. https://doi.org/10.1039/B306105C.

(26) Health and Safety Executive. *Metals and Metalloids in Air by X-Ray Fluorescence Spectrometry*; MDHS91/2; Health and Safety Executive, 2014. https://www.hse.gov.uk/pubns/mdhs/pdfs/mdhs91-2.pdf.

(27) Harper, M.; Demange, M. Analytical Performance Criteria: Concerning Sampler Wall Deposits in the Chemical Analysis of Airborne Metals. *Journal of Occupational and Environmental Hygiene* **2007**, *4* (9), D81–D86. https://doi.org/10.1080/15459620701493149.

(28) ISO. *Workplace Air - Determination of Hexavalent Chromium in Airborne Particulate Matter - Method by Ion Chromatography and Spectrophotometric Measurements Using Diphenyl Carbazide*; Standard 16740:2005; International Organization for Standardization, 2005. https://www.iso.org/obp/ui/#iso:std:iso:16740:ed-1:v1:en.

(29) ASTM International. *Standard Test Method for the Determination of Hexavalent Chromium in Workplace Air by Ion Chromatography and Spectrophotometric Measurement Using 1,5-Diphenylcarbazide*; ASTM International, 2024.

(30) Ashley, K.; Applegate, G. T.; Marcy, A. D.; Drake, P. L.; Pierce, P. A.; Carabin, N.; Demange, M. Evaluation of Sequential Extraction Procedures for Soluble and Insoluble

Hexavalent Chromium Compounds in Workplace Air Samples. *J. Environ. Monit.* **2009**, *11* (2), 318–325. https://doi.org/10.1039/B812236A.

(31) Madler, S.; Sun, F.; others. Trace-Level Analysis of Hexavalent Chromium in Lake Sediment Sample Using Ion Chromatography Tandem Mass Spectrometry. *Journal of Environmental Protection* **2016**. https://doi.org/10.4236/jep.2016.73037.

(32) Chen, Z.; Megharaj, M.; Naidu, R. Removal of Interferences in the Speciation of Chromium Using an Octopole Reaction System in Ion Chromatography with Inductively Coupled Plasma Mass Spectrometry. *Talanta* **2007**, *72* (5), 948–952. https://doi.org/10.1016/j.talanta.2007.05.030.

(33) Quartles, C. D.; Szoltysik, M.; Sullivan, P.; Reijnen, M. A Fully Automated Total Metals and Chromium Speciation Single Platform Introduction System for ICP-MS. *Journal of Analytical Atomic Spectrometry* **2019**, *2*, 284–291. https://doi.org/10.1039/C8JA00342D.

(34) EPA. *Method 218.6: Determination of Dissolved Hexavalent Chromium in Drinking Water, Groundwater, and Industrial Wastewater Effluents by Ion Chromatography*; EPA Method; Environmental Protection Agency, 1994. https://www.epa.gov/sites/production/files/2015-08/documents/method_218-6_rev_3-3_1994.pdf.

(35) EPA. *Method 218.7: Determination of Hexavalent Chromium in Drinking Water by Ion Chromatography with Post-Column Derivatization and UV-Visible Spectroscopic Detection*; EPA Method; Environmental Protection Agency, 2011. https://nepis.epa.gov/Exe/ZyPDF.cgi?Dockey=P100GH3E.txt.

(36) Thermo Fisher Scientific. *Changes from EPA Method 218.6 to 218.7 Yield Improved Detection Limits for Hexavalent Chromium*; Thermo Fisher Scientific, 2019. https://assets.thermofisher.com/TFS-Assets/CMD/Reference-Materials/ar-ic-epa-method-changes-hexavalent-chromium-column-0212-en.pdf.

(37) Michalski, R.; Jabloska, M.; Szopa, S.; Lyko, A. Application of Ion Chromatography with ICP-MS or MS Detection to the Determination of Selected Halides and Metal/Metalloids Species. *Critical Reviews in Analytical Chemistry* **2011**, *41* (2), 133–150. https://doi.org/10.1080/10408347.2011.559438.

(38) Seby, F.; Gagean, M.; Garraud, H.; Castetbon, A.; Donard, O. F. X. Development of Analytical Procedures for Determination of Total Chromium by Quadrupole ICP-MS and High-Resolution ICP-MS, and Hexavalent Chromium by HPLC-ICP-MS, in Different Materials Used in the Automotive Industry. *Analytical and Bioanalytical Chemistry* **2003**, *377* (4), 685–694. https://doi.org/10.1007/s00216-003-2133-5.

(39) EPA. *Elemental and Molecular Speciated Isotope Dilution Mass Spectroscopy*; SW-846 Update V EPA Method 6800; Environmental Protection Agency, 2014. https://www.epa.gov/sites/production/files/2015-12/documents/6800.pdf.

(40) Huang, L.; Yu, C. H.; Hopke, P. K.; Shin, J. Y.; Fan, Z. Trivalent Chromium Solubility and Its Influence on Quantification of Hexavalent Chromium in Ambient Particulate Matter Using EPA Method 6800. *Journal of the Air & Waste Management Association* **2014**, *64* (12), 1439–1445. https://doi.org/10.1080/10962247.2014.951745.

(41) Meiha, J.; Mester, Z. Paradigms in Isotope Dilution Mass Spectrometry for Elemental Speciation Analysis. *Analytica Chimica Acta* **2008**, *607* (2), 115–125. https://doi.org/10.1016/j.aca.2007.11.050.

(42) Pantsar-kaillio, M.; Manninen, P. K. G. Optimizing Ion Chromatography-Inductively Coupled Plasma Mass Spectrometry for Speciation Analysis of Arsenic, Chromium and Bromine in Water Samples. *International Journal of Environmental Analytical Chemistry* **1999**, *75* (1–2), 43–45. https://doi.org/10.1080/03067319908047299.

(43) Thermo Fisher Scientific. *Speciation Analysis of Cr(III) and Cr(VI) in Drinking Waters Using Anion Exchange Chromatography Coupled to the Thermo Scientific iCAP Q ICP-MS*; AU 40398; Thermo Fisher Scientific, 2019. https://assets.thermofisher.com/TFS-Assets/CMD/Application-Notes/AN-43098-ICP-MS-Chromium-Drinking-Water-AN43098-EN.pdf.

(44) Tirez, K.; Silversmit, G.; Bleux, N.; Adriaensens, E.; Roekens, E.; Servaes, K.; Vanhoof, C.; Vincze, L.; Berghmans, P. Determination of Hexavalent Chromium in Ambient Air: A Story of Method Induced Cr(III) Oxidation. *Atmospheric Environment* **2011**, *45* (30), 5332–5341. https://doi.org/10.1016/j.atmosenv.2011.06.043.

(45) Tirez, K.; Brusten, W.; Cluyts, A.; Patyn, J.; De Brucker, N. Determination of Hexavalent Chromium by Species Specific Isotope Dilution Mass Spectrometry and Ion Chromatography–1,5-Diphenylcarbazide Spectrophotometry. *J. Anal. At. Spectrom.* **2003**, *18* (8), 922–932. https://doi.org/10.1039/B302313C.

(46) Thermo Fisher Scientific. *Determination of Hexavalent Chromium in Drinking Water Using Ion Chromatography*; AU 144; Thermo Fisher Scientific, 2019. https://assets.thermofisher.com/TFS-Assets/CMD/Application-Notes/4242-AU144_LPN1495.pdf.

(47) NIOSH. *NIOSH 7303: Elements by ICP (Hot Block/HCl/HNO3 Digestion)*; Manual of Analytical Methods NMAM Fourth Edition; National Institute for Occupational Safety and Health, 2003. https://www.cdc.gov/niosh/docs/2003-154/pdfs/7303.pdf.

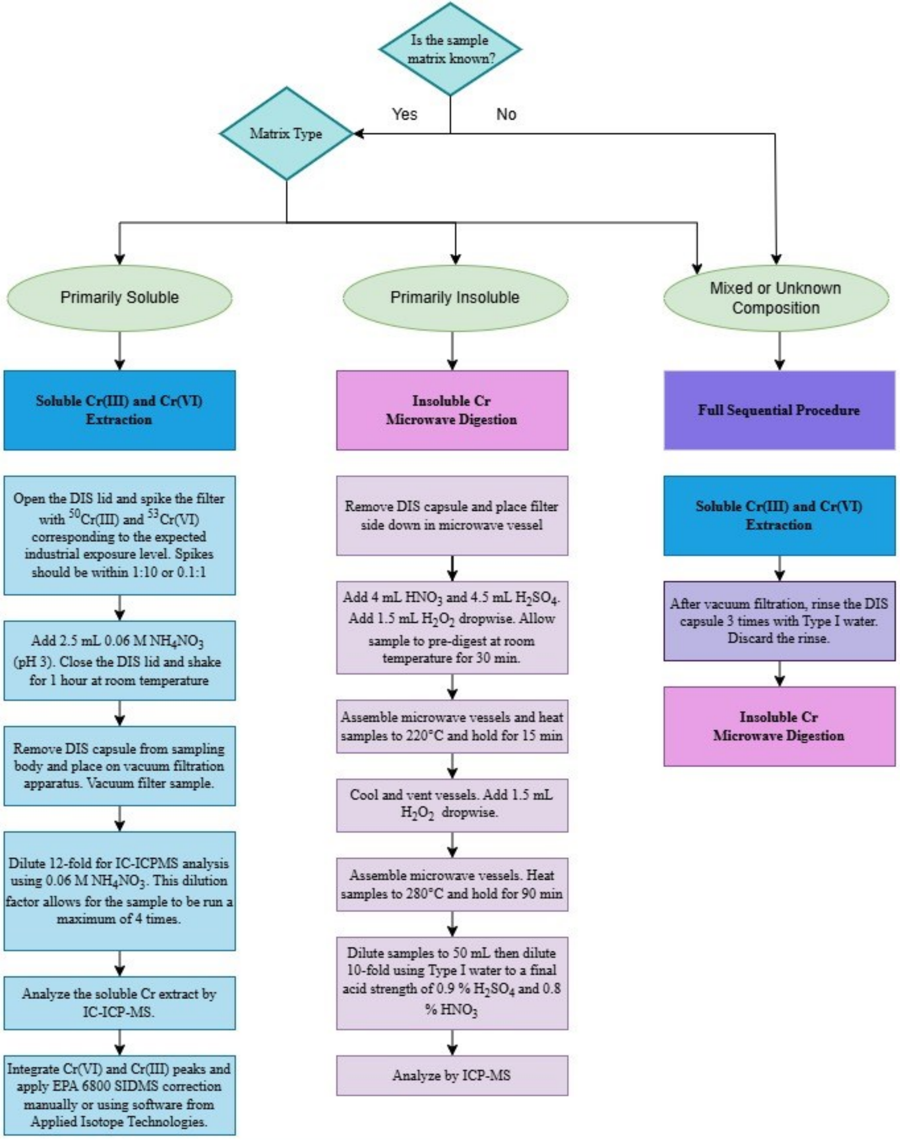
(48) NIOSH. *NIOSH 7304: Elements by ICP (Microwave Digestion)*; Manual of Analytical Methods NMAM Fifth Edition; National Institute for Occupational Safety and Health, 2014. https://www.cdc.gov/niosh/docs/2003-154/pdfs/7304.pdf.

(49) ISO. *Workplace Air - Determination of Metals and Metalloids in Airborne Particulate Matter by Inductively Coupled Plasma Atomic Emission Spectrometry - Part 2: Sample Preparation*; Standard 15202-2:2020; International Organization for Standardization, 2020.

(50) Butler, O.; Musgrove, D.; Stacey, P. Preparation and Certification of Two New Bulk Welding Fume Reference Materials for Use in Laboratories Undertaking Analysis of Occupational Hygiene Samples. *Journal of Occupational and Environmental Hygiene* **2014**, *11* (9), 604–612. https://doi.org/10.1080/15459624.2014.889301.

(51) ISO. *Workplace Air — Metals and Metalloids in Airborne Particles — Requirements for Evaluation of Measuring Procedures*; Standard 21832:2018; International Organization for Standardization, 2018.

Appendix



IC-ICP-MS Conditions Used for Soluble Cr Speciation	
Column	Dionex IonPac AG7 (50 mm x 4 mm, 10 µm) (PEEK)
Flow Rate	1 mL/min
Column Heater	30°C
Eluent	0.4 M HNO_3 (pH 4)
Sample Loop	1000 µL
Acquisition Mode	Time-Resolved Analysis
Flow Gas	Plasma 15 L/min
Power RF	1500 W
Reaction Gas	3 mL/min He
Analytical Masses (Dwell Time)	^{50}Cr (0.75 s), ^{52}Cr (0.75 s), ^{53}Cr (0.75 s)
Total Acquisition Time	5 min

ICP-MS Conditions for Insoluble Cr	
Nebulizer	Ezylok Micromist
Sampler cone	Nickel
Skimmer cone	Nickel
Acquisition Mode	Spectrum (Multi Tune)
Flow Gas	Plasma 15 L/min
Power RF	1500 W
Reaction Gas	3 mL/min He
Analytical Masses (Dwell Time)	^{52}Cr (0.75 s), ^{55}Mn (0.1 s), ^{57}Fe (0.1 s), ^{60}Ni (0.5 s), ^{66}Zn (0.5 s)
Internal Standards (Dwell Time)	^{7}Li (0.5 s), ^{45}Sc (0.2 s), ^{72}Ge (0.1 s), ^{89}Y (0.1 s), ^{115}In (0.1 s), ^{159}Tb (0.1 s)

Figure A1: Sequential analytical procedure for soluble Cr(VI) and Cr(III) extraction and insoluble Cr microwave digestion

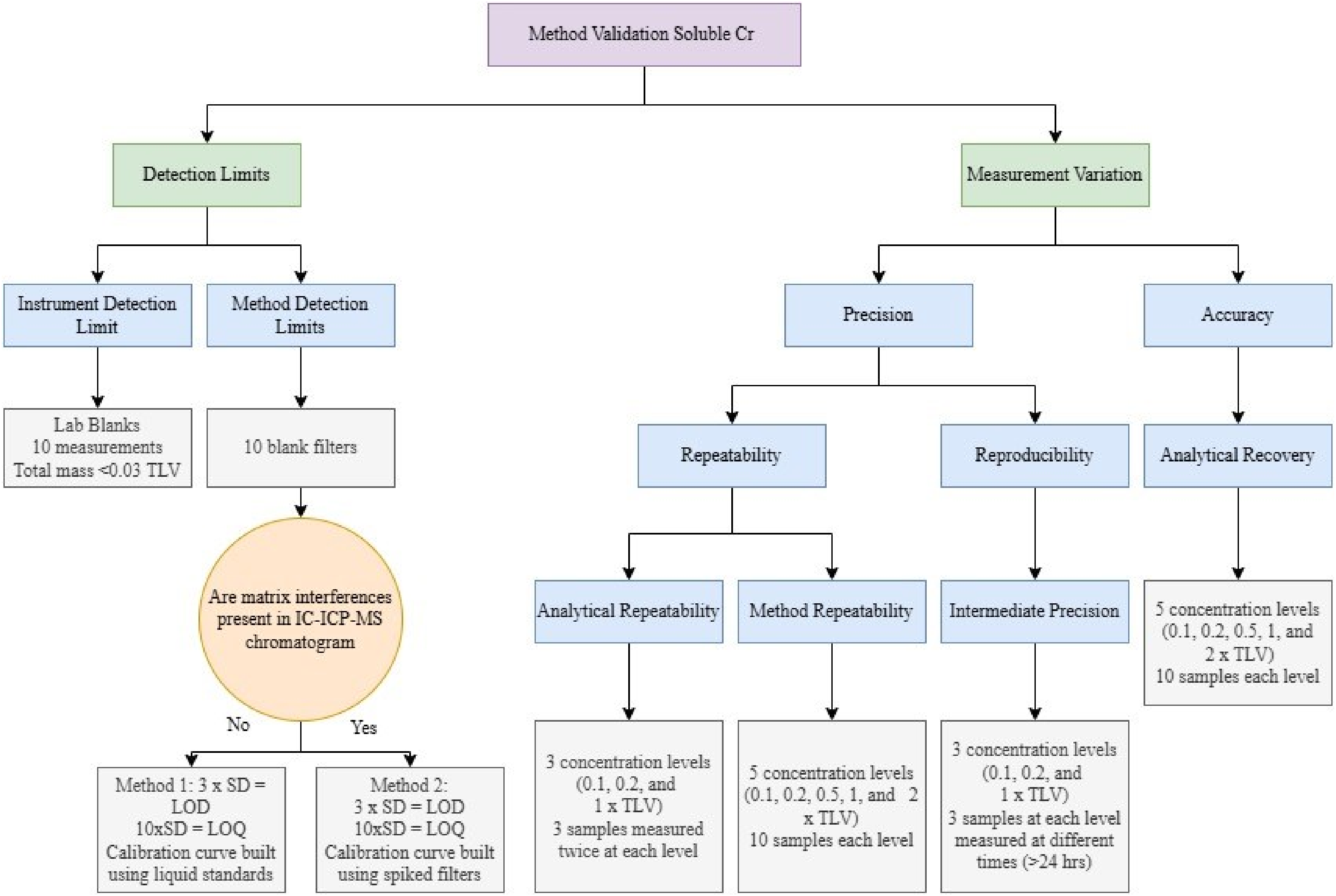


Figure A2: Method validation plan for soluble Cr(III) and Cr(VI) extraction and analysis by IC-ICP-MS

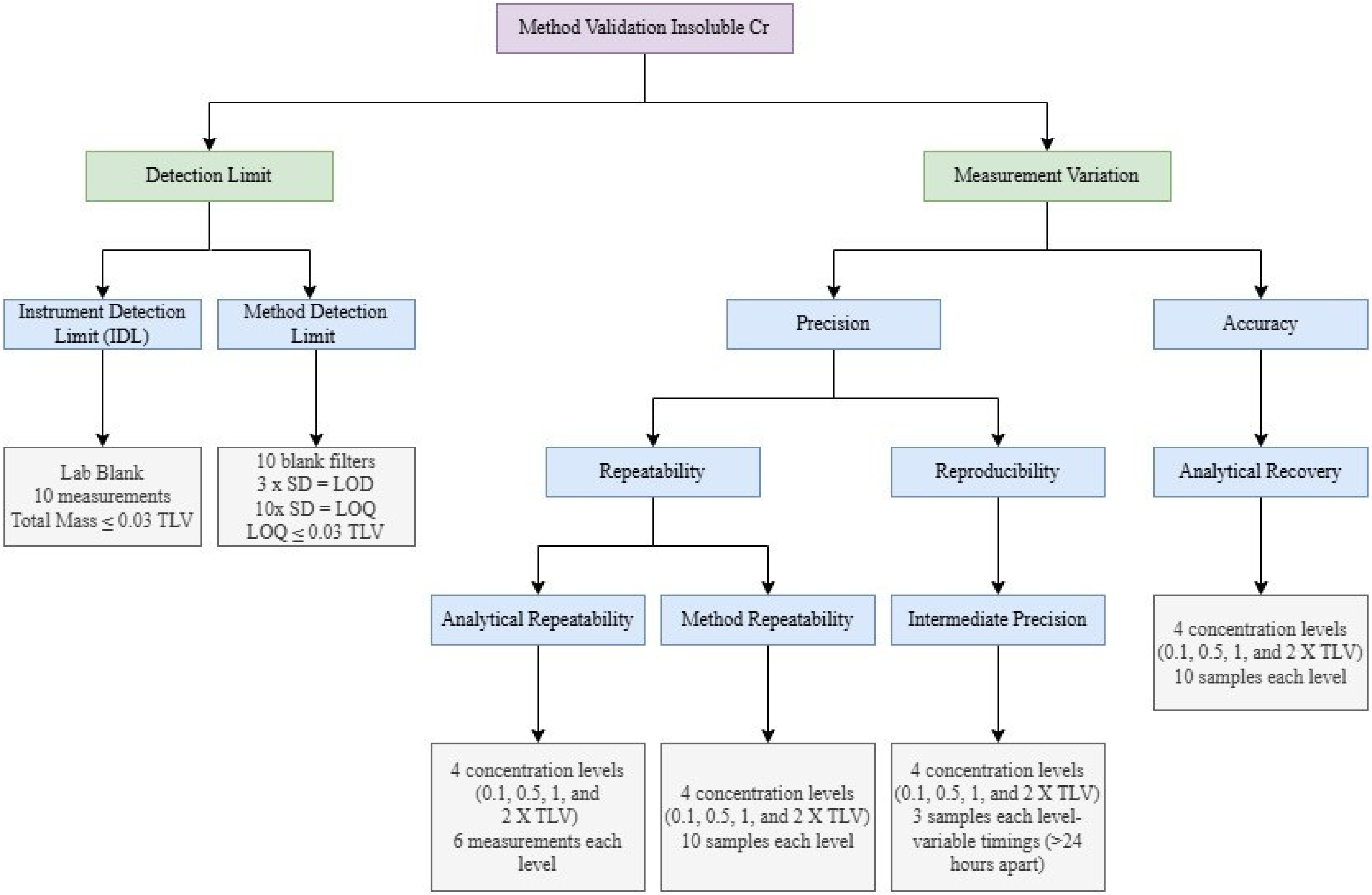


Figure A3: Method validation plan for insoluble chromium microwave digestion and analysis by ICP-MS