TUNGSTEN AND COBALT IN WORKPLACE ATMOSPHERES (ICP ANALYSIS)

Method Number:	ID-213
Matrix:	Air
OSHA Permissible Exposure Limits	
* Final Rule Limits	
Insoluble Tungsten (Insol. W):	5. mg/m^3 Time Weighted Average (TWA)
	10. mg/m^3 Short-Term Exposure Limit (STEL)
Soluble Tungsten (Sol. W):	1. mg/m^3 TWA
	3. mg/m^3 STEL
Cobalt (Co):	0.05 mg/m^3 TWA
Transitional Limits	
Insol. and Sol. W:	Not Applicable (NA)
Co:	0.1 mg/m^3 TWA
Collection Device:	An air sample is collected on a 37-mm mixed-cellulose ester (MCE) filter using a calibrated sampling pump and a 37-mm sampling cassette. Wipe and bulk samples can also be taken.
Recommended Sampling Rate	
TWA and STEL:	2. liters per minute (L/min)
Recommended Air Volumes	
TWA (W and Co):	480. L
STEL (W):	30. L
Analytical Procedure:	The MCE filter is subjected to a sequence of digestion steps using ammonium hydroxide (aqueous ammonia), water, hydrochloric acid, nitric acid, and phosphoric acid. The resulting solution is analyzed by aspiration into the argon stream of an inductively coupled plasma atomic emission spectrometer (ICP-AES).

Detection Limit (mg/m^3)

Qualitative:	W	Co	
TWA (W and Co)	0.0043	0.0003	
STEL (W)	0.069		
Quantitative:			
TWA (W and Co)	0.022	0.0017	
STEL (W)	0.34		
* Precision and Accuracy (TWA):	Insol. W	Sol. W	Co
Validation Ranges (mg/m^3):	2.5 - 10.0	0.5 - 2.0	0.025 - 0.10
CV (pooled):	0.045	0.0097	0.027
Bias:	+ 0.012	+ 0.073	+ 0.046
Overall Error (OE):	± 10.2%	± 9.2%	± 10.0%
Precision and Accuracy (STEL):	Insol. W	Sol. W	
Validation Level (mg/m^3):	10.0	3.0	
CV:	0.020	0.0070	
Bias:	+ 0.047	+ 0.062	
Overall Error:	± 8.7%	± 7.6%	

Method Classification:	Validated Method
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* Note: The U.S. Court of Appeals, Eleventh Circuit, recently decided that the Final Rules of the Air Contaminants Standard (29 CFR 1910.1000) be vacated. The Federal Occupational Safety and Health Administration (OSHA) enforcement would follow the "Transitional Limits" of Tables Z-1-A, Z-2, and Z-3 in effect before 1989. At that time, cobalt (Co) was regulated at an OSHA Permissible Exposure Limit (PEL) of 0.1 mg/m^3. In the case of tungsten (W), both soluble and insoluble W were regulated as nuisance dusts at a PEL of 15 mg/m^3 or potentially by reference to Section 5(a)(1) of the Occupational Safety and Health Act of 1970 and subsequent NIOSH 1977 recommendations for an insoluble W Recommended Exposure Limit (REL) of 5 mg/m^3 and a soluble W REL of 1 mg/m^3 (5.1.). References to PELs in this method refer to the Final Rule PELs. This method is applicable for determining compliance to either Final Rule or Transitional PELs.

1. Introduction

This method describes the sample collection and analysis of airborne tungsten (W) and cobalt (Co). Most industrial exposures to W also involve exposures to Co (5.1). Tungsten carbide (WC or W$_2$C) materials used for abrasives and cutting tools are frequently made containing Co metal which adheres to the surface of the hard but brittle tungsten carbide grains and cements them together into a tough composite. Other common components of cemented tungsten carbide materials include intermetallic compounds of W and Co (e.g., Co$_6$W$_6$C) in addition to other metals and their carbides. Because Co often occurs at significant levels in these materials, it is potentially present in airborne dusts along with W when tungsten carbide composites are used in the workplace. The Co component of cemented tungsten carbides has often been attributed as the etiological agent for certain occupational diseases observed in the tungsten carbide industry (5.1, 5.2). For these reasons, the sampling and analysis of Co was included in this method. Air samples are taken in the breathing zone of workplace personnel. Wipe and bulk samples can also be taken. Analysis is performed for elemental W and Co by Inductively Coupled Plasma Atomic Emission Spectrometry (ICP-AES).

During abrasive cutting or grinding, the matrix being cut or ground can aerosolize in addition to the grinding agent itself. The method is also suitable for screening other elements such as Al, As, Be, Ca, Cd, Cr, Cu, Fe, Mg, Mn, Mo, Ni, Pb, Sb, Se, Si, Sn, Te, Ti, V, Zn, and Zr.

1.1 History

Prior to this method, several analytical approaches of W particulates were used.

1.1.1 Atomic Absorption Spectroscopy (AAS)

Tungsten samples were digested by NIOSH Method P&CAM 271 (5.3) and analyzed by AAS. The high AAS detection limit (DL) for W limited its utility and the acid extraction of interferences such as Fe and Co introduced sources of sample loss. The use of hydrofluoric acid (HF) required the use of expensive Teflon labware and presented a potential hazard to the analyst. Because of these limitations, samples submitted for the analysis of W were often screened using qualitative X-ray Fluorescence (XRF) to determine if analysis was necessary or whether other analytes might be of greater interest to the industrial hygienist.

1.1.2 Direct Current Plasma Atomic Emission Spectroscopy (DCP-AES)

When DCP-AES became available, a modification of the P&CAM 271 AAS procedure (5.3) was tried by OSHA using two different digestion techniques. Analysis was by DCP-AES at a wavelength of 207.91 nm (5.4). In this modified procedure, mixtures containing WC, Co, and Fe powders were prepared using microwave digestion that gave recoveries of 95% for W (ranging from 92% to 99%), 77% for Fe, and 84% for Co. Samples digested in a fume hood in open Teflon beakers gave recoveries of 82% for W (ranging from 68 to

100%), 89% for Fe, and 87% for Co. The Co recoveries were disappointing, especially when considering its PEL (0.05 mg/m^3) and toxicity. Cobalt is considered more toxic than W (5.2)

1.1.3   X-ray Fluorescence (XRF)

Although an initial recovery study looked promising, attempts to validate an XRF technique using samples of various sieved W-containing materials deposited on silver membranes met with mixed success; thin-layer deposition presentations occasionally tended to be too uneven for adequate analytical precision to be realized. Because particle size can affect XRF recoveries, materials used in the validation were sieved to < 41 µm. Unfortunately, the necessity of sieving tungsten carbide composites complicated the interpretation of the results. Unlike stoichiometric compounds, the tungsten carbide composites consist of mixtures of particles of differing composition; therefore, it was uncertain whether the composition of the sieved material was still comparable to the certified composition (5.5).

1.1.4   Inductively Coupled Plasma Atomic Emission Spectroscopy

The next methodology investigated was ICP-AES. An in-house ICP instrument at the OSHA Salt Lake Technical Center (SLTC) was configured with W and Co channels.   The W and Co channels offer excellent detection limits. Additional channels included those necessary for potential interferences and channels to screen for other elements which may also be present in the workplace.

Attempts to validate an ICP-AES method for W and Co using a potassium pyrosulfate fusion sample preparation were unsuccessful; although dissolution of diverse W matrices appeared complete, the salt content resulting from the fusion caused high reflected power levels in the plasma chamber resulting in instrument shutdown. While such solutions might be analyzed for Co by AAS, W could not be effectively analyzed by AAS due to its high detection limit.

In pursuing digestion techniques, a procedure for the determination of Fe in bulk samples of tungsten carbide matrices was found (5.6.) which offered the potential of digesting tungsten carbide under relatively mild digestion conditions to produce a final solution consisting of a 6% phosphoric acid (H_3PO_4) matrix. Additional reagents and steps were needed, and the digestion procedure was adjusted until six diverse W matrices were completely digested. A final matrix of 2% H_3PO_4 in water was selected as being adequate for samples.

1.2   Principle

Samples are collected in the workplace using classical monitoring equipment and techniques. Sampling is further detailed in Section 2.

The wide variety of W matrices found in industry requires use of a sequence of digestion steps in sample preparation. The chemical principles involved in the digestion are detailed at the appropriate steps in the procedure in Section 3.5.

Digested samples are analyzed by aspiration into an inductively coupled argon plasma. This technique uses a high-power radio frequency (rf) source to power a water-cooled coil (inductor) around the end of the plasma torch. A high-voltage source initiates the plasma by causing some of the argon gas to ionize. The presence of ions renders it conductive. The high electrical power induced in the conductive plasma heats it to very high temperatures (5,000 to 8,000 K), and is capable of producing atomic and ionic emission lines (spectra) of elements aspirated into the argon stream.

The instrument currently in use at the OSHA-SLTC uses a diffraction grating and photomultiplier tube (PMT) system to isolate and quantitate the plasma-produced emissions. Light from the atomic

emissions passes into the optical system of the simultaneous atomic emission spectrometer and is dispersed into lines by a diffraction grating. This technique offers the opportunity to use analytical lines from higher order diffraction spectra to improve resolution and decrease the potential for interference. This instrument is set up to use primarily second and third order diffraction lines. Unwanted overlapping lines from other diffracted orders are reduced using optical filters. The light for various lines is detected simultaneously by an array of especially-aligned PMTs. Each PMT represents an analytical channel. Resolution is limited, so spectral overlap of lines of other elements is potentially present in the sample matrix. Two steps are taken to solve this problem:

1) Analytical channels are selected which minimize interferences so that normally only large amounts of interfering elements must be present before significant interference is observed.

2) Additional analytical channels that monitor for the presence of interfering elements are included in the analysis so that interelement corrections (IECs) can be readily made.

See Table 16 in Section 4.3 for a listing of the channels, wavelength, orders, and interferences used in this method.

1.3 Advantages and Disadvantages

1.3.1 This method has adequate sensitivity, accuracy, and precision for determining compliance with the OSHA Short-Term Exposure Limits (STEL) of W and the OSHA Time Weighted Average Permissible Exposure Limits (TWA-PELs) of W and Co.

1.3.2 Digestion conditions are surprisingly mild and the final solution matrix is dilute 2% H_3PO_4 reducing potential matrix effects.

1.3.3 The use of HF is avoided. This acid was commonly used in the past for W matrix digestions and required Teflon ware. Therefore, this method should be compatible with common silica glass ICP torch and nebulizer assemblies, and should be significantly safer for the analyst.

1.3.4 This method screens for many other elements that could be present in the workplace.

1.3.5 Pending further validation, Fe and Ni may also be analyzed by this method. This digestion matrix should be suitable for the analysis of these elements by either ICP-AES or AAS.

1.3.6 A disadvantage is the need to separately determine both soluble and insoluble W when both are known to be present in the workplace. See Table 7 in Section 1.6 for solubility designations for various common materials used in industrial applications.

1.3.7 Another disadvantage is the long digestion time required.

1.4 Method Performance

An Applied Research Lab (ARL) Model 3560 Atomic Emission Spectrometer with accompanying software (ARL, Sunland, CA) was used to determine method performance. Uncorrected results from the computer of the ARL Model 3560 were captured via a VAX 850 and networked to a personal computer (PC). Custom in-house software was used on the PC to perform iterative interelement corrections and produce reports. The additional software performed several functions including the following:

a) Speed the workup of data
b) Provide the ability to assess different interelement correction algorithms without need to reanalyze the samples
c) Avoid a "bug" found in the manufacturer's software (5.7)
d) Present the results in a form amenable to reporting samples

A synopsis of method performance is presented below. Further information can be found in Section 4.

1.4.1   This method was validated for spiked MCE filter samples corresponding to air concentrations of 0.025 to 1.41 mg/m^3 Co and 0.50 to 10.3 mg/m^3 W. See Sections 4.5. to 4.8. for details.

1.4.2   The qualitative detection limits (2 × SD) are shown in Table 1:

Table 1

Co	W	Assumptions
0.0032 µg/mL	0.041 µg/mL	
0.16 µg	2.1 µg	50 mL soln. vol.
0.0003 mg/m^3	0.0043 mg/m^3	480 L air vol.
0.0053 mg/m^3	0.069 mg/m^3	30 L air vol.

See Table 16 in Section 4.3 for qualitative detection limits of the screening elements.

1.4.3   The quantitative detection limits (10 × SD) are shown in Table 2 below:

Table 2

Co	W	Assumptions
0.016 µg/mL	0.21 µg/mL	
0.80 µg	10.3 µg	50 mL soln. vol.
0.0017 mg/m^3	0.022 mg/m^3	480 L air vol.
0.027 mg/m^3	0.34 mg/m^3	30 L air vol.

1.4.4   The sensitivity of the analytical method [(KPulse units per 1 µg/mL), KPulse is an integration unit used by a specific manufacturer of ICP instruments] was determined for W and Co while using the instrumental parameters listed in Table 10 (Section 4) and Table 16 (Section 4.3). The calibration is applicable over the analytical range shown. Above the analytical range, detector saturation can occur. The sensitivity is the slope of the calibration curve using the calibration range listed in Table 3:

Table 3

Element	Sensitivity	Calibration Range	Analytical Range
Co	3.8	0 to 10 µg/mL	0 to 200 µg/mL
W	1.0	0 to 100 µg/mL	0 to 1,000 µg/mL

1.4.5 The total pooled coefficients of variation (CV_T), biases, and OE for sample masses expected at about 0.5, 1, and 2 times the OSHA TWA PEL (Sections 4.5.-4.7.) are listed in Table 4 below:

Table 4

TWA			
Element	CV_T	Bias	OE (%)
Co	0.027	+ 0.046	± 10.0
W (Insol.)	0.045	+ 0.012	± 10.2
W (Sol.)	0.0097	+ 0.073	± 9.2

The OE (5.8.) was calculated using the equation:

$$OE_i = \pm(|bias_i| + 2CV_i) \times 100\% \quad \text{(95\% confidence level)}$$

Where *i* is the respective sample pool being examined. Air volumes of 480 L/min were used in calculating masses.

The results shown in Table 5 below were obtained using amounts approximating the Final Rule STEL concentrations (Section 4.5-4.6):

Table 5

STEL			
Element	CV_T	Bias	OE (%)
W (Insol.)	0.020	+ 0.047	± 8.7
W (Sol.)	0.0070	+ 0.062	± 7.6

An air volume of 30 L was used to calculate masses found near STEL determinations.

When sampling cemented tungsten carbides, Co is potentially present in amounts that greatly exceed the Co PEL when W is near its PEL. For this reason, additional Co analyses were performed in the evaluation of this method to ensure that quantitation of Co can be performed at the higher levels. The total pooled coefficients of variation (CV_T) and biases for samples analyzed for Co from 3.2 to 28 times the OSHA Final Rule PEL (Section 4.8) are listed in Table 6:

Table 6

High Concentration Co			
Element	CV_T	Bias	OE (%)
Co	0.018	+ 0.028	± 6.5

Bias and overall error (OE) values were calculated from those found analytically versus theoretical (known or certified) values.

1.4.6 Sample stability: No stability problems are expected in the case of matrices involving insoluble forms of W and Co. Some very soluble compounds of W, particularly sodium tungstate, may absorb enough water from the air to dissolve and penetrate into the backup pad. A procedure to stabilize such samples is presented in Section 2.2.6.

1.5 Interferences

1.5.1   There are no known chemical interferences.

1.5.2   Spectral interferences depend on the selection of wavelengths of the element channels (listed in Table 16 in Section 4.3). In the case of this analytical method, W and Co spectrally interfered slightly with one another when using the wavelengths recommended by the instrument manufacturer. In addition, Ti [present in some tungsten carbide matrices as titanium carbides (5.1)] interfered slightly with both W and Co. Additional elements of interest to industrial hygienists which might be present in tungsten carbide grinding operations (and elements interfering with the analysis of W and Co) were included for use in performing interelement corrections and screening. Also see Section 4.3 for more details regarding spectral interferences.

1.5.3   This method includes the analysis of Co, W, and the 22 screening elements listed in Section 1. The industrial hygienist should note the identity of additional elements suspected to be present in the workplace atmosphere so the analyst can evaluate the potential for possible interference.

1.6   Sources of Potential Exposure to W (CAS 7440-33-7) and W Materials Containing Co (CAS 7440-48-4) (5.1, 5.2, and 5.9) are listed in Table 7:

Table 7

Material	Application
Tungsten (Insol. W)	Welding electrodes, alloys, high speed tool steels, filaments in incandescent lamps, heating elements, rocket nozzles, and solar energy devices
Tungsten carbide (Insol. W)	Abrasive, cemented carbide tools, dies, and wear-resistant parts
Tungsten disulfide (Insol. W)	Solid lubricant
Tungsten carbonyl (Insol. W)	Deposition of tungsten coatings
Tungsten chlorides and fluorides (includes both Insol. W and Sol. W)	
Tungstic acid and tungsten oxide (Insol. W)	Textiles, ceramics, and plastics
Sodium tungstate (Sol. W)	Biological assays, fire proofing and waterproofing fabrics
Cobalt	Component in cemented tungsten carbide composites and alloys

1.7   Physical and Chemical Properties of W and Co (5.2):

Table 8 displays properties of the elemental forms of W and Co. Compounds and alloys containing these elements are also regulated under the OSHA PELs.

Table 8

Property	W	Co
Atomic weight	183.85	58.9332
Specific gravity	19.3	8.92
Melting point (°C)	3410	1493
Boiling point (°C)	5927	3200
Vapor pressure (torr)	non-volatile at room temp.	
Aqueous solubility	insoluble	

1.8   Toxicology (5.2, 5.10)

Note: Information listed within this section is a synopsis of current knowledge of the physiological effects of W and Co and is not intended to be used as a basis for OSHA policy.

Tungsten

1.8.1   When ingested or given intravenously to guinea pigs, the chief effects of W (insoluble) and $Na_2WO_4.2H_2O$ (soluble) are anorexia, colic, weight loss, incoordination of movement, trembling, and dyspnea (5.2).

1.8.2   The toxic effects of W are greater for the more soluble forms. In terms of W content, the compounds Na_2WO_4, WO_3, and $(NH_4)_6W_7O_{24}$ were shown to have decreasing toxicity to rats in the order listed. Insoluble WC was found biologically inert, although the metal W produced toxic effects. Dust chamber exposures of animals to W, WO_2, and WC produced only minor changes (5.2). The major toxic component in many tungsten carbide cutting tools is often the Co that provides the tough matrix in which the relatively brittle WC is embedded (5.1).

1.8.3   Reports of occupational effects from exposures to soluble W compounds are not found in the literature (5.1, 5.2).

Cobalt

1.8.4   Toxic response to Co often involves hypersensitivity. Pulmonary involvement in humans has been observed to lead to chronic interstitial pneumonitis. Effects on the lungs are often reversible. However, acute exposures to levels below 1 to 2 mg/m^3 have been fatal. Allergic dermatitis has also been observed in humans (5.2).

1.8.5   In the mineral assay and hard metal industries, human exposures to Co have been associated with non-inflammatory cardiomyopathy leading to heart failure. Elevated levels of Co were present in the heart tissue (5.11).

1.8.6   Cardiomyopathy and elevated Co levels in human heart tissue has also been found in beer-associated exposures to Co (from Co salts added as foam enhancers by some breweries during the 1960s). Of those who developed cardiomyopathy, 43% died. Exposures ranged from 1.0 - 1.5 µg/mL Co in beer that was ingested at a rate of 8 - 30 pints / day for a period of years (0.04 - 0.14 mg per kilogram body weight per day). The protein deficient diets of beer drinkers may have contributed. Cardiac effects have not been seen in people treated for anemia with 1 mg Co per kilogram body weight (5.10).

1.8.7   In guinea pigs, obliterative bronchiolitis adenomatosis is observed when high doses of cobalt are injected intratracheally. Animal studies appear to confirm hypersensitivity but do not necessarily model human lung responses (5.2).

2.   Sampling

2.1   Equipment

2.1.1   Mixed-cellulose ester (MCE) filters (0.8-µm pore size), cellulose backup pads, and cassettes, 37-mm diameter, part no. MAWP 037 A0 (Millipore Corp., Bedford, MA) are used. Cassettes, MCE filters, and backup pads of 25-mm diameter can also be used.

Note: Polyvinyl chloride (PVC) filters are applicable for analysis if only soluble forms of W or Co are suspected. See Table 7 in Section 1.6. for solubility designations of materials in various common industrial applications. See reference 5.1. for any materials not listed in Section 1.6. Insoluble forms of W or Co collected on PVC cannot be analyzed by this method, but may be analyzed gravimetrically in the field and may also be submitted for "Qualitative XRF" analysis (OSHA Method no. ID-204) for elements present (atomic numbers 13-92 which include W and Co). Always submit blank samples for any analysis.

2.1.2   Gel bands (Omega Specialty Instrument Co., Chelmsford, MA) for sealing cassettes.

2.1.3   Calibrated personal sampling pumps capable of sampling within ±5% of the recommended flow rate of 2 L/min.

2.1.4   Various lengths of polyvinyl chloride tubing to connect sampling cassettes to pumps.

2.1.5   A stopwatch and bubble tube or meter to calibrate pumps.

2.1.6   Smeartabs (part no. 225-24, SKC Inc., Eighty Four, PA) for wipe sampling.

2.1.7   Scintillation vials, 20 mL, (part no. 74515 or 58515, Kimble, Div. of Owens-Illinois Inc., Toledo, OH) with polypropylene or Teflon liners for bulk and wipe sampling. See Section 2.3 for details.

2.2   Sampling Procedure − Air Samples (5.1)

Collect samples on 0.8-μm pore size, 37-mm diameter MCE filters. Conduct the particulate sampling with the filter cassette located within the breathing zone of the employee.

Note: Some welding operations involve W. If a welding operation is being sampled for W, conduct the welding fume sampling with the MCE filter cassette located inside the welding helmet. If the free-space inside the hood precludes the use of 37-mm diameter cassettes and MCE filters, 25-mm sampling assemblies with MCE filters can be used.

2.2.1   Place a MCE filter and a cellulose backup pad in each two- or three-piece cassette. Seal each cassette with a gel band.

2.2.2   Prepare at least one blank for each batch of ten samples. Use the same lot of MCE filters for blank and collected samples. Handle the blank filters in the same manner as the samples except that no air is drawn through blanks.

2.2.3   Calibrate each personal sampling pump with a prepared cassette in-line to approximately 2 L/min flow rate.

2.2.4   Attach prepared cassettes to calibrated sampling pumps (the backup pad should face the pump) and place in appropriate positions on the employee or in the workplace area. For STEL samples, use a flow rate of 2 L/min and a minimum sampling time of 15 min. For TWA determinations, take two consecutive 480-L samples at a flow rate of 2 L/min for 240 min each.

Note: If other regulated soluble compounds (e.g., Cr^{2+}, Cr^{3+}, soluble salts of Al, Fe, Mo, Ni, $ZnCl_2$, etc.) are suspected to be present in the sampled air, take separate samples. Request analysis for the specific regulated compound(s). These samples are analyzed using OSHA Method No. ID-121 and not by this method.

2.2.5   If the filter becomes overloaded while sampling, another filter cassette should be prepared. Consecutive samples using shorter sampling periods should be taken if overloading occurs. After sampling, place plastic end caps tightly on both ends of the cassette.

2.2.6   Special instructions for soluble W samples: Prudent precautions should be used to stabilize certain air samples after collection. In humid air, some soluble W compounds are deliquescent, i.e., they can absorb water vapor from humid air and form a solution. Such solution formation on a filter could spread to the backup pad (which is not analyzed) resulting in low recoveries.   For soluble W samples:

1) Open the cassette.

2) Carefully lift out the MCE filter with forceps. Do not disturb any of the particulate on the filter.
3) Remove and discard the backup pad.
4) Replace the MCE filter in its original orientation.

Apply OSHA 21 seals in such a way as to secure the end caps. Record the sampling conditions. Treat the blank(s) in the same way. For air samples on MCE filters that are suspected of containing only soluble W, request "Soluble W." Otherwise, request "Soluble and Insoluble W" analysis on the OSHA 91A. Ship air and blank samples to the lab. Cobalt results will be reported in addition to the requested W analysis.

2.2.7   Instructions for air samples not containing soluble W: Apply OSHA 21 seals in such a way as to secure the end caps. Record the sampling conditions. Specify "W+Co" analysis and ship air and blank samples to the laboratory. When "W+Co" is requested, soluble W will not be reported.

2.2.8   When other compounds are known or suspected to be present in the air, such information should be transmitted with the sample. This is particularly important for elements not included among the 22 screened elements listed in Section 1. Other more exotic elements may produce spectral interferences in the analysis of W and Co. The industrial hygienist should note the identity of additional elements suspected to be present in the workplace atmosphere so that the analyst can evaluate possible interferences.

2.3   Bulk Samples and Wipe Samples

Very finely divided bulk material can be analyzed by this method. Settled dust samples are preferred. The laboratory may not be able to grind coarse samples of many of the hard industrial W matrices to a fine enough particle size for digestion by this method. As an alternative for bulk analysis, OSHA Method ID-204 may be used to assess the surface composition of bulk samples. If there are any questions about bulk sampling for W or Co, call the OSHA SLTC.

Wipe samples taken on smear tabs may be submitted for analysis. **Do not collect wipe samples using PVC filters, large Whatman filters, or backup pads**.

2.3.1   Bulks: Place bulk samples in 20-mL scintillation vials. Fill 20-mL scintillation vials at least half full. Large pieces that do not fit inside 20-mL scintillation vials may be shipped in larger containers.

2.3.2   Wipes: Prepare at least one blank for every ten wipe samples.

1) Wear clean, impervious, disposable gloves when taking each wipe sample.
2) Moisten the wipe filters with deionized water prior to use.
3) If possible, wipe a surface area covering 100 cm^2.
4) Fold the wipe sample with the exposed side in.
5) Transfer the wipe sample into a 20-mL scintillation vial, seal with a cap having an inert plastic liner, and wrap with vinyl or electrical tape. Securely wrap an OSHA-21 seal length-wise (top to bottom) around the vial.

2.3.3.   Complete the OSHA Form 91A. See Table 7 in Section 1.6 for solubility designations for materials in various common industrial applications. Specify "W+Co", "Soluble W", "Soluble and Insoluble W" and/or "Qualitative XRF" analyses as appropriate and ship the bulk and wipe samples to the laboratory separately from air samples.

3. Analysis

3.1   Safety Precautions

3.1.1   Refer to appropriate ICP-AES instrument manuals and the standard operating procedures (SOP) for proper instrument operation (5.12, 5.13).

3.1.2 Observe laboratory safety regulations and practices.

3.1.3 The reagents $NH_{3(aq)}$ (NH_4OH), HCl, HNO_3, and H_3PO_4 are corrosive. Use appropriate personal protective equipment such as safety glasses, goggles, splash shield, gloves, and lab coat when handling corrosive chemicals. Prepare solutions in an exhaust hood.

3.2 Equipment

3.2.1 Inductively coupled plasma atomic emission spectrometer (ARL Model 3560 or equivalent configured with channels Co, W, and major interferant elements).

3.2.2 Automatic sampler, if desired.

3.2.3 Laboratory computer system for data reduction, if desired.

3.2.4 Filtering apparatus for extractions: vacuum system or aspirator, assorted hoses, trap, suction flask, filtering stand, filtering funnel, clamp, wash bottle, and container to receive filtrate.

3.2.5 Miscellaneous volumetric ware: Pipettes; micropipettes; 50-1,000 µL pipette tips* (such as part no. RC-200, Rainin Instrument Co., Inc., Woburn, MA); volumetric flasks; Erlenmeyer flasks; graduated cylinders; and beakers.

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* Note: Concentrated H_3PO_4 is syrupy and wets glass. To deliver aliquots of H_3PO_4 quantitatively and reproducibly, use a plastic pipette tip that is not appreciably wetted by H_3PO_4.

3.2.6 Parafilm.

3.2.7 Forceps.

3.2.8 Plastic wrap or aluminum foil.

3.2.9 Thermostated hot plate(s) 70 to 100 °C and 180 to 200 °C.

3.3 Reagents

All chemicals should be at least reagent grade. Refer to Material Safety Data Sheets (MSDSs) for safe and proper handling of reagents.

3.3.1 Reagents:

Deionized water (DI H_2O).
Ammonium hydroxide (NH_4OH) ($NH_{3(aq)}$), concentrated (28.6% as NH_3).
Hydrochloric acid (HCl), concentrated (36.5 - 38.0%).
Nitric acid (HNO_3), concentrated (70.9%).
Phosphoric acid (H_3PO_4), concentrated (85.5%).

3.3.2 ICP stock standards:

The stock standards used in the validation are listed in Table 11 in Section 4. All calibration standards are prepared from 1,000 µg/mL ICP stock standards (except for the 10,000 µg/mL Fe standard). Atomic spectral (ICP) standards may be used. Standards normally classified as "atomic absorption" may not be appropriate due to the presence of contaminants. Stock standards prepared in water, dilute nitric acid, and dilute hydrochloric acid matrices are suitable provided that they do not cause precipitation when mixed together to prepare calibration standards.

3.4   Preparation of Standards

Table 9 below summarizes the preparation of standards. All the calibration standards and the reagent blank use a final 2% H_3PO_4 matrix except for the 1,000 µg/mL solution of Ti. The 1,000 µg/mL Ti stock standard is used neat (without any added H_3PO_4) because a high concentration of Ti in 2% H_3PO_4 tends to produce a precipitate after several hours. Prepare the calibration standards (except Ti) in 100-mL volumetric flasks containing 2 mL H_3PO_4 and about 25 mL DI H_2O.

The ICP stock solutions listed in Table 11 in Section 4. were compatible when mixed together at the dilutions used in preparing the standards listed below. If substitutions for these stock solutions are made, different combinations for standards may be necessary in order to avoid possible precipitation reactions, (e.g., do not mix together ICP stock solutions containing SO_{42-} and Pb^{2+}). After adding the aliquots of ICP stock standards, dilute to 100 mL with DI H_2O. Mix thoroughly.

Immediately transfer the standard which contains the silicon standard (labelled "4" in Table 9 below) to a plastic bottle. The other standards may be stored in glass volumetric flasks.

Table 9

Label	ICP Stock Standards	mL	Final Concentration (µg/mL)
Acid	none	NA	0 (reagent blank)
1	Be, Cd, Co*, Cu, Pb, Zn	0.200	2.00 each
2	Cr, Mo, Ni, Sb, V, Fe	0.200	2.00 each and 20.00 for Fe
3	Ca, Mg, Mn, Al, As, Se, Te	0.200	2.00 each
4	Sn, Si, Zr	1.00	10.00 each
W	W*	10.00	100.0
Co	Co**	1.000	10.00
Ti	Ti	NA	1,000.

*   Tungsten solutions are not stable for long periods (<3 months).
**   A three point calibration curve is used for Co; two point calibration curves are used for the other elements.

3.5   Sample Preparation

A flow chart is shown in Figure 1 to assist the analyst in preparing samples. Observe laboratory safety rules. Use personal protective equipment necessary to conduct safe acid digestions and a laboratory exhaust hood appropriate for acid use when preparing samples and glassware.
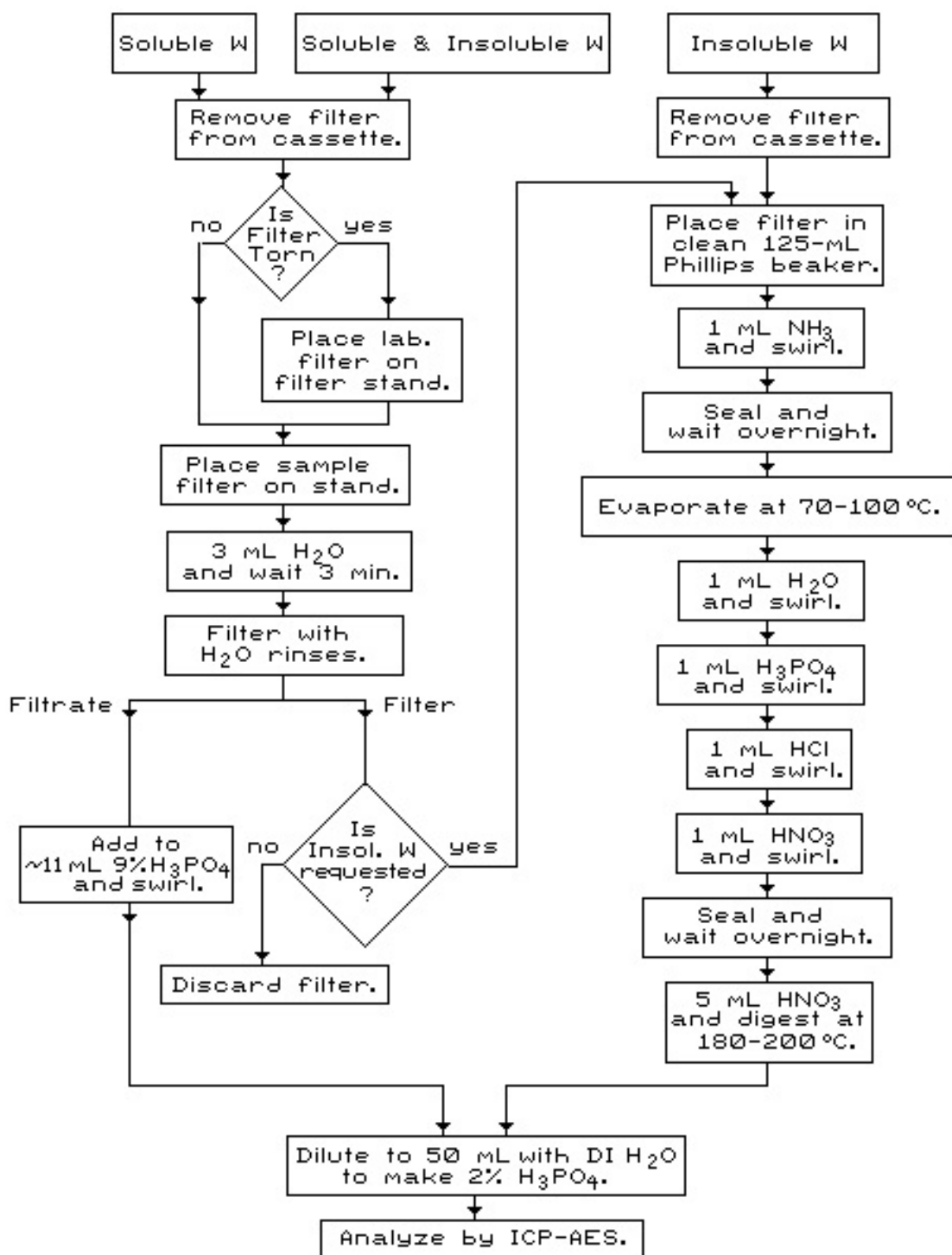
Soluble W

Soluble & Insoluble W

Insoluble W

Remove filter from cassette.

Remove filter from cassette.

Is Filter Torn ? no yes

Place filter in clean 125-mL Phillips beaker.

Place lab. filter on filter stand.

1 mL NH$_3$ and swirl.

Seal and wait overnight.

Place sample filter on stand.

Evaporate at 70-100 °C.

3 mL H$_2$O and wait 3 min.

1 mL H$_2$O and swirl.

Filter with H$_2$O rinses.

1 mL H$_3$PO$_4$ and swirl.

Filtrate   Filter

1 mL HCl and swirl.

1 mL HNO$_3$ and swirl.

Add to ~11 mL 9% H$_3$PO$_4$ and swirl.

Is Insol. W requested ? no yes

Seal and wait overnight.

Discard filter.

5 mL HNO$_3$ and digest at 180-200 °C.

Dilute to 50 mL with DI H$_2$O to make 2% H$_3$PO$_4$.

Analyze by ICP-AES.

Figure 2 Overview of Tungsten Air Sample Preparation. Notes: The source of NH$_3$ is NH$_4$OH. The sample volume for samples containing insoluble W is reduced to 1 mL on the hotplate before final dilution to 50 mL with DI Water.

3.5.1   Glassware cleaning

1)   Clean 125-mL Phillips beakers to be used for sample digestions by refluxing with 1:1 HNO_3 in an exhaust hood. Rinse well with DI H_2O.
2)   Rinse the 50- and 100-mL volumetric flasks with 10% HNO_3. Rinse well with DI H_2O.

3.5.2   Soluble W air sample preparation.

Note: It is often possible to determine by the nature of the operation that only soluble W or only insoluble W may be present. (See Table 7 in Section 1.6. for solubility designations of various common tungsten materials in industrial applications.) In such cases where only one solubility designation applies, the separate extraction and analysis of soluble W is not necessary. For example, grinding operations using cemented tungsten carbides normally need not be analyzed for soluble W.

1)   Carefully remove the filter from the polystyrene cassette with forceps and place the sample filter, dust side up, on the moistened platform of a filtering apparatus. Secure the filtering funnel, and add 3-mL DI H_2O.

Note: If the sample filter is torn, place the filter on the filtering stand on top of a laboratory 0.8-μm pore size MCE filter. (If insoluble W is requested, combine filters. For corresponding blank corrections, combine a field and laboratory blank.)

Allow to stand for 3 minutes. (See Section 3.5.3. step 2 regarding treatment of contaminated backup pads.)
2)   Apply vacuum while supplying several mL of DI H_2O from a wash bottle to quantitatively transfer the solution to a receiving container.
3)   Quantitatively transfer the solution from the receiving container to a clean 50-mL volumetric containing 1 mL H_3PO_4 in about 10 mL DI H_2O. Dilute to volume with DI H_2O and mix well.
4)   If insoluble W is also requested, carefully place each extracted filter in a clean labelled 125-mL Phillips beaker so that it rests on the bottom of the beaker.

Note: Care should be exercised to avoid getting the filter or filter fragments up on the glass beaker where digestion will be inefficient.

5)   For the soluble portion, proceed to Section 3.6 below.
6)   For the insoluble portion, proceed to Section 3.5.3, steps 2 to 11.

3.5.3   Insoluble W air sample preparation.

Complete sample digestion of certain insoluble W matrices requires reaction times for steps 3 and 8 listed below that exceed the analyst's normal 8-h workday. For this reason, overnight reaction times are indicated for these two steps. If less time is given for digestion, low recoveries are observed. To avoid unexpected complications, it is important to observe both the sequence of operations and the hot-plate temperature ranges given in the digestion procedure. For example, excessive or prolonged heating (i.e., far beyond the endpoint indicators described in the associated note) in the final digestion may allow the H_3PO_4 to dissolve some of the silica in the Pyrex Phillips beaker and complicate the analysis by producing a phosphosilicic acid gel. No significant concentrations of Si were found when this method was validated using the procedure stated below. In the unlikely event that a gel forms, transfer the suspension to transparent plastic ware and try clearing the gel with the minimum drop-wise addition of HF.

Note: Use extreme caution in handling concentrated HF. Hydrofluoric acid is both corrosive and toxic. It is particularly hazardous because it rapidly penetrates deep below intact skin and causes extensive tissue damage. Check first aid procedures before using.   Cleanup spills promptly with appropriate spill cleanup materials.

Observe laboratory safety rules.   Use personal protective equipment and an appropriate laboratory exhaust hood when preparing samples.

1) Carefully remove the filter from the polystyrene cassette with forceps.
2) Transfer each sample filter into a clean labelled 125-mL Phillips beaker so that it rests on the bottom of the beaker. If dust collected during sampling no longer adheres to the filter and is found on the inside walls of the cassette, carefully rinse out the insides of the cassette into the appropriate beaker with a few mL of DI H_2O.

Note: Care should be exercised to avoid getting the filter or filter fragments up on the glass beaker where digestion will be inefficient.

Contaminated backup pads may be analyzed in the manner of MCE filters with the additional treatment noted in step 10 below. If analysis of contaminated backup pads is performed, also analyze the backup pad of the blank so that blank corrections may be performed.

3) In an exhaust hood, add 1 mL of concentrated $NH_{3(aq)}$ to each Phillips beaker and quickly seal the tops of the Phillips beakers with Parafilm followed by plastic wrap or aluminum foil. Allow to stand overnight.

Note: The concentrated $NH_{3(aq)}$ weakens MCE filters and dissolves any WO_3 to form soluble tungstate. The WO_3 matrix is not soluble in the acid digestion steps used in this method. Some Co in samples containing cemented tungsten carbides may also dissolve as a result of air oxidation and complexation of Co by NH_3. The minimum practical volume of concentrated $NH_{3(aq)}$ to use in this step is 1 mL. Concentrated $NH_{3(aq)}$ tends to evaporate readily; therefore, to avoid loss of NH_3 and speed the process, the plastic wrap and Parafilm should be cut to size before the aqueous $NH_{3(aq)}$ is added. More $NH_{3(aq)}$ (2 mL total) could be used if desired because the excess is removed in step 4. Be consistent in the volume of $NH_{3(aq)}$ used for samples and blanks. The H_3PO_4 used in Step 6 dissolves any remaining insoluble tungsten-containing dust; it complexes both the ferric iron and the tungstates that form during digestion.

4) After standing overnight, the sealed beakers should still contain liquid. If no liquid is present, the previous step must be repeated (including allowing it to stand overnight) because the ammonia may have evaporated before the reaction was complete.

Note: If Co is present in sufficient amounts, a purple or brown solution may result.

Uncover the beakers and quickly evaporate the remaining liquid in an exhaust hood on a hot-plate at 70 to 100 °C. Remove from the hot plate and cool to room temperature.

5) Add 1 mL DI H_2O or distilled H_2O (to dissolve soluble tungstates and prevent dehydration to insoluble tungstic acid when the acids are added). Swirl to dissolve soluble components; some Co complexes present may decompose to a brownish mass during the gentle heating in the previous step but will quickly dissolve in subsequent steps when the acids are added.

6) Add 1 mL of H_3PO_4. Swirl to mix well.

7) Add 1 mL of HCl. Swirl. A blue $[CoCl_4]^{2-}$ complex may form.

8) Add 1 mL of HNO_3. Swirl. Seal the beakers with Parafilm (or cover with watch glasses) and allow to stand overnight.

Note: The low viscosity of this mixed acid matrix solution is important in dissolving the residual Co out of the tungsten carbide composites. Diffusion is limited in these matrices; the formation of both slightly soluble tungstates and gas bubbles formed during the digestion may clog the passages between the carbide grains. It takes time for the H_3PO_4 to diffuse between the grains and complex any tungstic acid that forms. Gaseous oxidants present in the solution are less soluble at elevated temperatures. This digestion is hindered if high temperatures are applied too soon; therefore, the samples are allowed to sit overnight for the reaction to take place.

9) Add 5 mL of HNO_3 to the samples and digest at 180 to 200 °C until the volume is reduced to approximately 1 mL (mostly H_3PO_4) and digestion is complete. Cool to room temperature.

Note: To determine completion of digestion (≈ 1 mL left), the 1 mL tends to draw away from the center because Phillips beakers have slightly raised centers. Completion is also evidenced by the following events: The reddish-brown fumes above the solution dissipate, and the golden solution turns colorless. The solution becomes viscous and ceases to bubble. If Co is present in a large amount, the solution may be slightly bluish when hot and very pale pink when cool.

10) To digest any backup pads that may be contaminated with sample, add 2 mL DI H_2O and swirl to mix well. Add 5 mL HNO_3 and repeat step 9 once more.

11) Point the mouth of the flask away from yourself. Slowly and cautiously add DI H_2O to the H_3PO_4 solution and transfer quantitatively to 50-mL volumetric flasks using DI H_2O rinses. Dilute to volume with DI H_2O and mix well.

3.5.4 Bulk sample preparation:

Prepare bulk samples by weighing 3 to 5 mg of each dry bulk sample on individual tared 0.8-μm pore size, 37-mm diameter, MCE filters that have reached constant weight. Record the weights. Transfer the filter containing the sample to a 125-mL Phillips beaker and prepare according to either Section 3.5.2 or 3.5.3 above. Also prepare a blank from the same lot of filters.

3.5.5 Wipe sample preparation:

Transfer each Smeartab wipe sample to individual 125-mL Phillips beakers and prepare according to either Section 3.5.2 or 3.5.3 above. Also prepare a blank from the same lot of Smeartabs.

3.6 Standard and Sample Analysis

Note: If particulate remains after digestion, the sample(s) should be filtered using a disposable-syringe-type Teflon filter(s) prior to analysis to prevent plugging the nebulizer.

1) Analyze the standards and reagent blank by ICP-AES. Calibrate the instrument and analyze samples according to the appropriate ICP instrument SOP (5.13). Instrument parameters used during this validation are listed in Table 10 in Section 4.
2) If necessary, analyze standard and reagent blanks to determine the detection limits using the appropriate manufacturer's software. ICP-AES detection limits normally do not vary significantly unless the instrument is altered through maintenance or abuse.
3) Analyze the samples, calibration standards, and blanks by ICP-AES.
4) Follow the SOP for further instructions regarding analysis (5.13).
5) Some samples require reanalysis. These include the following:
   a) Dilute and reanalyze any samples which have calculated concentrations above the analytical range. This especially includes samples which saturate (overdrive) any channels. Evidence for overdriven channels may vary, and is described further in the ICP SOP for the particular instrument (5.13). Pipet an appropriate aliquot of the high concentration sample into a clean volumetric flask and dilute to volume with 2% H_3PO_4.
   b) Reanalyze any samples and corresponding blanks if results indicate a high degree of imprecision . This problem is evidenced by a high relative standard deviation (CV > 10%) of the three exposure measurements/sample.

3.7 Calculations

3.7.1 Perform interelement corrections. According to the equation below, a final concentration for each analyte is calculated:

$$C_c \; = \; C_{unc} \; - \; \sum (K_i \times C_i)$$

where:
C_c = corrected concentration of an element
C_{unc} = uncorrected concentration of the element
C_i = concentration from each contributing interference for the element
K_i = respective Interelement Correction (IEC) factor for the interference

Application of this equation is an iterative process described in greater detail in Section 4.3. These corrections are calculated either "real-time" using software provided by the instrument manufacturer or post-analysis using custom software.

3.7.2   Obtain hard copies of the data and results from a printer.

3.7.3   The amount of analyte in each sample or blank is calculated as:

μg A = (μg/mL A) × (mL S) × (DF)
where:
μg A = Total μg of analyte in the sample or blank
μg/mL A = Measured concentration of analyte in solution (derived from calibration curve)
mL S = Total volume of the solution analyzed
DF = Amount of dilution applied to an aliquot of the original solution (ratio of final volume divided by the aliquot volume)

3.7.4   The blank value, if any, is subtracted from each sample:

$$\mu g_c\ A = (\mu g\ A) - (\mu g_b\ A)$$

where:
μg_c A = μg of analyte, blank corrected
μg A = μg of analyte from equation in Section 3.7.3 above
μg_b A = μg of analyte in blank

Wipe samples are reported in terms of μg of analyte.

3.7.5   For air samples, calculate mg/m^3 exposures for all screened elements, Co, soluble W, and insoluble W:

$$mg/m^3\ A\ =\ \frac{(\mu g_c\ A)\ \times\ (GF)}{L}$$

where:
GF = Gravimetric factor
L   = Air volume in liters

For those elements having a PEL listed as an oxide, the gravimetric factors are calculated from formula weights (FW):

GF = 1.2447 for FW_{ZnO}/FW_{Zn}
GF = 1.4298 for $FW_{Fe2O3}/2FW_{Fe}$
GF = 1.7852 for $FW_{V2O5}/2FW_{V}$

3.7.6   Compare the calculated mg/m^3 exposures to the various PELs or OSHA action limits. Evaluate the reliability of the results for all detected elements whose air concentration may exceed a PEL or an action limit. With the custom software available at the OSHA SLTC, the analytical results reported for each sample includes a listing of the total interelement correction and the corrected concentration for each element detected in the sample.

3.7.7   Convert bulk sample analytes to % composition using:

$$\%\ A\ =\ \frac{(\mu g_c\ A)\ \times\ (100\%)}{(mg\ B)\ \times\ (1000\ \mu g/mg)}$$

where:
mg B = milligrams of bulk sample

3.8   Reporting Results

3.8.1   When evidence of migration of the sample to the backup pad is observed on any air sample, advise the industrial hygienist that part of the sample was collected on the backup

pad. When this occurs, report the sum of exposure results for the air filter sample and the corresponding backup pad.

3.8.2   Report exposures in terms of mg/m^3 as appropriate for Co, soluble W, and insoluble W.

3.8.3   Discuss high exposures of screened elements with your supervisor and the industrial hygienist. Resubmit air samples and blanks for additional confirmation and quantitation of any screened elements near or over the PEL, or discuss resampling with the industrial hygienist. Include copies of sampling information and results when resubmitting samples.

4. Backup Data

This analytical method has been validated for the spiked MCE filters specified in Section 2.1.1.   The method validation was performed according to guidelines (5.14, 5.15) with the exception of the sampling validation. The analytical method validation was conducted at the respective OSHA Final Rule TWA-PELs and STELs for W and Co. Several reasons precluded aerosol sampling validation.

a)   Aerosol generation of cemented tungsten carbides is very difficult because of the high density of this matrix. The great hardness of this material precludes grinding to a smaller particle size range.
b)   The generation of cemented tungsten carbide aerosols of known composition is not feasible because cemented tungsten carbides are non-stoichiometric.
c)   The non-stoichiometric nature of cemented tungsten carbides makes the generation of uniform dispersions of aerosol of known composition infeasible.
d)   Equipment to generate and measure aerosols was not available at the time of this validation.

Instrument parameters used during validation are listed in Table 10 below. (Additional information regarding this instrument may be found in reference 5.7):

Table 10

The Specifications for the ARL 3560 Simultaneous ICP-AES			
RF GENERATOR:		Snout Gas Flow (L/min)	1.5
Generator (Model No. Henry)	2.5 kW *	Nebulizer Uptake Rate (mL/min)	2.3
Incident Power (W)	1,175	Nebulizer type	Meinhard-Type A
Reflected RF Power (W)	0-20	Peristaltic Pump Used? (yes/no)	no
P.A. Plate Supply Voltage (V)	4,100	Pre-Integration Flow Time (s)	30
P.A. Plate Current (mA)	700	Integration Time (s)	5
P.A. Grid Current (mA)	125	Number of Exposures	†
P.A. Filament Voltage (V)	7.5	SPECTROMETER:	
P.A. Tune (Setting)	190	Instrument Model	3560
P.A. Load (Setting)	050	Grating (lines/mm)	1,080
(where P.A. = Power Amplifier)		Primary Slit Size (µm)	20
EXCITATION:		Profiling Element	Mn
Plasma Observation Height (mm)	15	Profile Point (peak dial div.)	496 ‡
Coolant Gas Flow (L/min)	12	Vacuum (µmHg)	20
Coolant Gas Pressure (psi)	25.5	Path Length (m)	1
Plasma Gas Flow (L/min)	0.8	COMPUTER CONFIGURATION:	
Plasma Gas Pressure (psi)	21.5	Disk Drive Capacity	30 Megabyte fixed 1.2 Megabyte 5.25 in. floppy
Carrier Gas Flow (L/min)	1	Computer System	Micro 11/53 DEC Computer
Carrier Gas Pressure (psi)	30.5	Software (operating system)	DPS/TSX+

*   Indicates peak rf power capability in kW.
†   Dependent on software program used; 10 for DL determinations, and 3 for calibrations and analyses.
‡   From spectral scanning device (SAMI). This value can change over time.

The instrument calibration standards were those listed in Table 11 below:

Table 11

ICP Stock Standards*	Matrix	ICP Stock Standards*	Matrix
Al	0.3 M HCl	Ni	0.3 M HNO_3
As	0.3 M HCl	Pb	0.3 M HNO_3
Be	0.3 M HCl	Sb	H_2O
Ca	0.3 M HNO_3	Se	0.3 M HNO_3
Cd	0.3 M HNO_3	Si	H_2O
Co	0.3 M HNO_3	Sn	2.5 M HCl
Cr	H_2O	Te	10% HCl
Cu	0.3 M HNO_3	Ti	H_2O
Fe	5% HNO_3	V	0.3 M HNO_3
Mg	0.3 M HNO_3	W	H_2O
Mn	0.3 M HNO_3	Zn	0.3 M HNO_3
Mo	H_2O	Zr	2% HNO_3

* All calibration standards are prepared from 1,000 µg/mL ICP stock standards (except for the 10,000 µg/mL Fe standard).

The method validation consisted of the following experimental protocol:

1)   Preliminary assessments of reference materials.
2)   Preliminary determination of W and Co analytical recoveries of diverse tungsten-containing matrices. Preparation and analysis of two spiked samples each of six different solid-phase tungsten-containing matrices representative of industrial exposures individually spiked on MCE filters. These studies included two different cemented tungsten carbide matrices containing Co.
3)   Determination of interelement corrections.
4)   Determination of the qualitative and quantitative detection limits and background equivalent concentrations.
5)   Determination of analytical method precision and accuracy for insoluble W. Preparation and analysis of spiked MCE filter samples of three samples each of the two most difficult insoluble matrices (94% WC/6% Co and 88% W_2C/12% Co) at W exposures at 0.5 ×, 1 ×, and 2 × TWA PEL. Preparation and analysis of six spiked MCE filter samples of pure W metal which represent concentrations of insoluble W near the STEL.
6)   Determination of analytical method precision and accuracy for soluble W. Preparation and analysis of spiked MCE filter samples of six samples each of soluble W ($Na_2WO_4 \cdot 2H_2O$) representing W exposures at 0.5 ×, 1 ×, and 2 × TWA PEL. Preparation and analysis of six spiked MCE filter samples which represent concentrations of soluble W near the STEL.
7)   Determination of analytical method precision and accuracy for Co. Preparation and analysis of solution-spiked MCE filter samples of six samples each of Co at 0.5 ×, 1 ×, and 2 × TWA PEL. These were also spiked with W to give a 100 µg/mL W solution matrix.
8)   Determination of analytical method precision and accuracy for Co at higher levels. Analysis of solution-spiked MCE filter samples of three samples each of Co at 3.2 ×, 6.5 ×, 7.4 ×, 12.3 ×, 14.9 ×, and 28.0 × TWA PEL.
9)   Assessment of typical levels of blank contamination, analyte carry-over, and noise. Preparation and analysis of four blank MCE filter samples for W and Co.
10)   Summary.

All analytical results were calculated from concentration-response curves, corrected for reagent blank and interelement interferences as identified in Section 4.3, and statistically examined. In addition, the analytical recoveries were tested for possible outliers using the Treatment of Outliers test (5.8). For samples tested at different levels, the appropriateness of pooling was tested by checking the homogeneity of variance using the Bartlett's test (5.17). Statistical evaluation was conducted according to Inorganic Methods Evaluation Protocol (5.14). To reduce cumulative round-off errors during calculations in this method, additional non-significant digits

were preserved in the intermediate results shown in the backup data in Section 4. Results shown in the main body of the method are shown rounded off to the correct number of significant figures.

4.1   Preliminary Assessment of Reference Materials:
In order to develop a method for measuring atmospheric exposures in the workplace, unsieved reference materials of six diverse common industrial tungsten-containing matrices were selected as models ($Na_2WO_4 \cdot 2H_2O$, WC, 94% WC/6% Co, 88% W_2C/12% Co, WO_3, and W).

Procedure

The cemented tungsten carbide matrices were manufacturer-labelled with nominal descriptions "88% W_2C/12% Co" and "94% WC/6% Co" indicating only the approximate elemental composition of these matrices. Certificates of Analysis provided accurate analytical results for certain major and trace elements. For the purpose of this validation, these matrices were further characterized by qualitative powder X-ray diffraction analysis to identify the crystalline phases of tungsten carbide actually present. Appropriate stoichiometric factors could then be calculated based on the information presented on the respective Certificates of Analysis.

Particle sizing for each of the six materials was also assessed based on product information, measurement, and visual inspection.

Results
X-ray Diffraction Analyses

The powder diffraction patterns corresponding to WC and Co were identified by X-ray diffraction analysis of the 94% WC/6% Co matrix. X-ray diffraction analysis results for this matrix were not reported on the Certificate of Analysis provided by the manufacturer.
    The powder diffraction patterns corresponding to WC, Co, and Co_6W_6C were identified in the 88% W_2C/12% Co matrix. The compound with the formula W_2C (suggested by the label 88% W_2C/12% Co) was not identified by X-ray diffraction analysis. The Certificate of Analysis for this matrix indicated that X-ray diffraction analysis had identified the major phase as WC, with traces of Co_6W_6C and Co_3W_3C. The compound W_2C was not listed on the Certificate of Analysis.
    The use of these materials in the validation offers an excellent opportunity to determine recoveries for chemically bound and interstitial elemental Co.

The Na$_2$WO$_4$·2H$_2$O was particle-sized using a 41 µm sieve and a metric ruler. It was found to consist primarily of granular crystalline material with particles in the size range of 41 µm to 1 mm. Particle sizing on the other materials was not performed because the manufacturer product descriptions of the particle size ranges were available. These descriptions are included in the Tables 12 to 15 in Section 4.2.

4.2   Preliminary Determination of W and Co Analytical Recoveries of Diverse Tungsten-Containing Matrices: This study was performed to test the matrix independence of the digestion procedure of this analytical method. Six diverse tungsten-containing matrices described in Section 4.1 were digested and analyzed. To ensure that the digestion procedure was compatible with the MCE filter used for sampling and would also have adequate capacity, several of these samples were spiked with amounts of reference material approaching 10 mg.

Because this method is based on the analysis of elemental composition, gravimetric conversion factors must be used to convert from the mass of a matrix spike to the mass of an analyte element. In order to accurately evaluate recoveries, the manufacturer's reagent label information and Certificates of Analysis were used to calculate the gravimetric factors listed in Tables 12 to 15 below. In addition to chemical formula information, these data included percent purity and, in some cases, elemental composition. For example, Na$_2$WO$_4$·2H$_2$O was listed as 100.4% pure based on tungsten content (presumably due to water of hydration lost during manufacture). In the case of the tungsten carbide matrices, the respective gravimetric factors implied by the nominal compositions 88% W$_2$C/12% Co and 94% WC/6% Co were in good agreement with the gravimetric factors calculated from the certification provided by the manufacturer.

Procedure

Matrix spikes were prepared from reagent and certified sources independent of calibration standards. Two samples of each of the six dry matrices were prepared. Known amounts of each dry sample matrix were added to individual tared 0.8-µm pore size, 37-mm diameter, MCE filters that had reached constant weight in a controlled low humidity lab environment (35% RH). All 12 samples were digested and analyzed according to this method using 50-mL solution volumes and the same ICP-AES instrument described at the beginning of Section 4. Because of their importance to the method, the tungsten carbide/Co samples were re-analyzed. Interelement interferences were noted and were corrected for the affect of Co on W and for W on Co. The details for determining these corrections are further discussed in Section 4.3. Interelement corrections were not performed on screened elements for this preliminary test because they were present in these materials at trace levels.

The amounts of W and Co in these analyte spikes were calculated from assay information provided by the chemical manufacturer. All W and Co results were calculated from concentration-response curves, corrected for reagent blank, corrected for interelement interferences between W and Co, and statistically examined.

Results

Results for the preliminary analyses for spiked W and Co samples are shown in Table 12 (repeat analyses of tungsten carbide/Co samples are tabulated separately):

Table 12

Tungsten Matrix Digestion Evaluation – Tungsten Results					
Matrix in 2% H$_3$PO$_4$	Amount (mg)	% W in Matrix	µg/mL Theory (T)	µg/mL Found (F)	W Recovery F/T
W, powder	2.446	100.00	48.92	49.72	1.0164
W, powder	4.769	100.00	95.38	96.30	1.0097
WO$_3$, powder	3.068	79.10	48.54	48.61	1.0014
WO$_3$, powder	6.121	79.10	96.83	95.00	0.9811
WC, ≤ 1 µm	3.496	93.40	65.31	65.83	1.0080
WC, ≤ 1 µm	3.637	93.40	67.94	69.37	1.0211

Matrix	Amount	% W in Matrix	µg/mL Theory	µg/mL Found	W Recovery F/T
94% WC, ≤ 45 µm	4.201	87.87	73.83	71.67	0.9708
94% WC, ≤ 45 µm	9.922	87.87	174.37	167.70	0.9618
88% W_2C, 5 to 45 µm	5.742	84.08	96.56	97.37	1.0084
88% W_2C, 5 to 45 µm	8.551	84.08	143.79	145.49	1.0118
$Na_2WO_4{\cdot}2H_2O$	2.401	55.96	26.87	27.07	1.0074
$Na_2WO_4{\cdot}2H_2O$	7.638	55.96	85.48	87.88	1.0280
$Na_2WO_4{\cdot}2H_2O$	9.684	55.96	108.38	106.50	0.9826
Average					1.0007
(SD = 0.0202) CV					±0.0202

The tungsten carbide spiked samples were reanalyzed for W confirming the recoveries obtained above. These results are shown in Table 13:

Table 13

Tungsten Matrix Digestion Evaluation – Tungsten Results (Repetitions)					
Matrix in 2% H_3PO_4	Amount (mg)	% W in Matrix	µg/mL Theory (T)	µg/mL Found (F)	W Recovery F/T
94% WC (repeat)	4.201	87.87	73.83	72.26	0.9788
94% WC (repeat)	9.922	87.87	174.37	166.61	0.9555
88% W_2C (repeat)	5.742	84.08	96.56	96.71	1.0016
88% W_2C (repeat)	8.551	84.08	143.79	145.05	1.0087
Average					0.9862
(SD = 0.0241) CV					±0.0244

The same tungsten carbide spiked samples were also analyzed on the ICP-AES instrument giving the Co recoveries shown in Table 14:

Table 14

Tungsten Matrix Digestion Evaluation – Cobalt Results					
Matrix in 2% H_3PO_4	Amount (mg)	% Co in Matrix	µg/mL Theory (T)	µg/mL Found (F)	Co Recovery F/T
94% WC, $\leq$ 45 µm	4.201	5.45	4.58	4.93	1.0766
94% WC, $\leq$ 45 µm	9.922	5.45	10.82	11.56	1.0689
88% W_2C, 5 to 45 µm	5.742	11.70	13.44	13.65	1.0159
88% W_2C, 5 to 45 µm	8.551	11.70	20.01	20.44	1.0215
Average					1.0457
(SD = 0.0314) CV					±0.0301

These samples were reanalyzed for Co confirming the recoveries shown above. The results of the Co reanalyses are listed in the Table 15:

Table 15

Tungsten Matrix Digestion Evaluation – Cobalt Results (Repetitions)					
Matrix in 2% H_3PO_4	Amount (mg)	% Co in Matrix	µg/mL Theory (T)	µg/mL Found (F)	Co Recovery F/T
94% WC (repeat)	4.201	5.45	4.58	4.96	1.0832
94% WC (repeat)	9.922	5.45	10.82	11.53	1.0661
88% W_2C (repeat)	5.742	11.70	13.44	13.53	1.0070
88% W_2C (repeat)	8.551	11.70	20.01	20.44	1.0215
Average					1.0445
(SD = 0.0361) CV					±0.0345

4.3   Determination of Interelement Corrections (IECs):

Spectral interferences in ICP-AES generally occur when weak lines of one or more interfering elements overlap the analytical line of another element. The configuration of 25 channels included in this method (2 Fe channels and 23 other channels) provides the opportunity to correct for up to 575 potential interferences (2 × 23 + 23 × 23 = 575). Significant interferences normally need to be corrected for by using interelement correction factors. The equation used to calculate IEC factors is:

$$K_i = B_i / C_i$$

where:
K_i = IEC factor for a particular pairing of affected element withaffecting element
B_i = apparent concentration determined on the channel of the affected element produced by aspiration of the single-element standard of the interference element
C_i = concentration of the interference element

These IEC factors are typically small. A typical factor of 2×10^{-4} means that a 1,000 µg/mL standard of the interferant produces a signal on the channel comparable to 0.2 µg/mL of the element represented by the channel. The determination of interelement correction factors requires the presence of large amounts of the interfering elements; therefore, the stock solutions used in the interference study have concentrations that far exceed levels expected in actual samples. The solutions used were of high purity

and expected to give reliable indications of interferences. However, interferences on the Si channel may not be as reliable due to contamination from Si in the glassware used in manufacture and preparation.

Spectral corrections are minimal for most screened elements but are included to avoid misleading indications of overexposures to screened elements. Interferences from matrix background and contamination are minimized by the experimental design. During calibration, a reagent blank is measured on all channels. The intercept of the resulting calibration curve therefore corrects for the reagent matrix background and for any contamination from the aqueous ammonia and reagent acids. When the MCE filter or Smeartab wipe sample medium contributes background, the blank sample media results can also be subtracted. When the sample dust matrix contributes to the background, only interferences from those elements measured on other channels can be corrected in this method. Spectral interferences on an affected line are corrected based on measurements at the analytical lines of known interferant elements. Most elements potentially present in W matrices are included in the list.

Background corrections were not applied in this method other than for intercept and blanks. Other approaches to background corrections are often provided by instrument manufacturers. Background interference corrections are sometimes performed by background modelling. The simplest model is to assume that the background level measured at a preselected wavelength near the affected line represents the background level "under" a peak signal. Such an approach considers the elevated background without regard to cause and requires a familiarity with the sample matrix for all samples to be analyzed. A wide variety of sample matrices may be problematic using this approach, unless each sample is scanned to determine that the background model is appropriate. It is an appropriate strategy if the background is known to be level across the ICP scan, and the selected background wavelength does not overlap spectral interference peaks of any other elements (not just screening elements). Such assumptions regarding background corrections may be inappropriate for matrices submitted for routine analyses by this method; therefore, that approach was not used.

A few interferences having an elevated background component were noted (such as the interference of W on the Co channel). In this method, both background and spectral interferences were treated as linear functions of the interfering element and are corrected as spectral interferences.

Once determined, the IEC factors are used in the iterative interelement correction equation given in Section 3.7.1. When the channels for interference elements do not have interferences from other elements; the measured concentrations of the interferant elements are accurate, and the corrections are first order and can be made in one step. Second and higher order interferences are common in ICP; interferences themselves often have interferences, and the initial estimates of interference element concentrations may be progressively corrected in an iterative process. In such a process, the concentrations of interference elements having interferences are progressively corrected so that the C_c of the interferant element resulting from the previous step substitutes for C_i in making corrections in the subsequent step. (C_{unc} in the equation does not change.) Estimates of concentrations of both analytes and interferences are improved at each step and the process is continued until there are no significant differences in concentrations of the elements calculated at each step or until the differences are less than the corresponding detection limits. The iterative process converges to an internally consistent set of results.

<u>Procedure</u>

For W, Co, and all screening elements, one or more standard solutions each containing 1,000 μg/mL of a single interferant element (10,000 μg/mL in the case of Fe) were analyzed, and apparent concentrations were measured on the other element channels for indications of interference. These stock solutions are listed in Table 11 in Section 4.

The analysis of high concentration standards can result in carry-over (See Section 4.9 for an evaluation of carry-over). To reduce the possibility of misidentifying minor carry-over between measurements as interference, the solutions of the elements were analyzed twice: first in (near) alphabetical order and then in reverse order. The lower of these two measurements was used to calculate the interference correction factors.

Archived scans for interferences on W and Co were visually examined to assess the types of interferences affecting the analysis of these elements and to help assess the appropriateness of using a linear model to correct for these interferences.

Results

The IEC factors for each interference noted were calculated as described in the introductory remarks above. These IEC factors are instrument dependent; for brevity, only a relative ranking of interferences is shown in Table 16 below along with pertinent channel parameters, qualitative DL, and background equivalent concentration (BEC) data (DL and BEC results are further discussed in Section 4.4). Interferences shown in **bolded type** have correction factors exceeding 10^{-4} expressed as µg/mL channel per µg/mL interferant. The range of interest for interference correction factors extends below 10^{-4} for certain elements; these additional detected interferences are indicated by element symbols in small type. Interferences are included without distinction to background or spectral type and are listed by element symbol in order of decreasing magnitude. Only significant interferences are shown and are corrected for. The cutoff criterion for determining significant interelement correction factors was whether an element, at a concentration of 100 µg/mL, would produce an apparent concentration on another element's channel exceeding 5% of the Final Rule Limit for that element (50-mL solution volume and 480-L air volume). The conservative criterion used to determine significance functions well with this configuration of channels selected for use in sampling W and Co in workplace atmospheres. The 100 µg/mL criterion is applied to individual interfering elements, whereas 100 µg/mL for a 50-mL solution volume corresponds to 5 mg material on the MCE filter which represents a high estimate of the total amount of all interfering and non-interfering elements likely to result from air sampling. The 5% criterion represents a small fraction of the PEL. In this method, the largest IEC factor used was 0.09255 [(µg/mL Fe)/(µg/mL Co)] for the interference of Co on the less sensitive Fe channel. The smallest non-zero IEC factor used in this method was 0.00001 [(µg/mL Be)/(µg/mL Ti)]. The W contained in the matrices used in the validation produces an Sb interference (K_i = 0.01431) which illustrates the importance in performing interelement corrections; as a worst-case example, a 100 µg/mL W solution produces a signal on the Sb screening channel indicating 1.4 µg/mL Sb (corresponding to approximately 0.25 × OSHA PEL for Sb).

Although an interference was noted for Ti on both W and Co determinations, in the absence of additional complexing agents (e.g., oxalate ion) any digested titanium would be converted to insoluble titanium phosphate. For this reason, the interference from titanium may be minimal. (Spot tests of various titanium compounds using the digestion procedure indicate that the anatase and rutile forms of TiO_2 are only slightly soluble, while titanium oxalate is completely soluble.) The instrument in use at the OSHA SLTC was not equipped with a Ti channel, but Ti could be monitored adequately on the Os channel (225.585 nm) where Ti strongly interferes. Titanium has a peak centered at 225.580 nm. Osmium is a very rare element that is not expected to be present in workplace atmospheres sampled for W and Co.

In addition to those listed, other potential interferences were identified in this study, but they were judged insignificant for the expressed purposes of this method.

Table 16

Channel	Wavelength (nm)	Order *	DL, µg/mL (2 × SD)	BEC, µg/mL	Interferences
			ICP-AES Instrumental Parameters and Observed Interferences		
Al	308.215	2	0.11050	6.32	**Be**
As	189.042	3	0.03150	1.30	**Si Mo Cr Al Be W** Fe1
Be	313.042	2	0.00055	0.0345	**V** Zr Ti
Ca	393.366	2	0.00040	0.0891	
Cd	226.502	3	0.00425	0.232	**Fe1 Ni** Mo As Ti Co Al W
Co	228.616	2	0.00320 (ID-213) 0.00850 (ID-125G)	0.569	**Ti W Cr Ni Cd Mg** Fe1 Mo Zr Be
Cr	267.720	3	0.01000	0.766	
Cu	324.754	2	0.01000	0.665	**Mo Cd**

Table 16

					ICP-AES Instrumental Parameters and Observed Interferences
Fe1	259.940	3	0.00600	0.431	
Fe2	271.440	3	0.16150	9.34	**Co**
Mg	279.080	2	0.10250	5.86	
Mn	257.610	3	0.00195	0.0680	
Mo	202.030	3	0.01200	0.495	
Ni	231.604	3	0.01600	0.649	
Pb	220.353	3	0.06500	2.44	**Al Ni W Co Zr Se Mn Cu Cd Zn Fe1**
Sb	217.581	3	0.06250	2.46	**W Be Zn**
Se	196.090	3	0.05150	2.52	**W Al Mn Sb**
Si	288.158	2	0.06550	3.52	**Sb Al W**
Sn	189.980	3	0.01800	0.877	
Te	214.275	2	0.06450	3.79	**V Cd Mo Ti Mg W Zn Al Fe1 Mn Cu**
Ti †	(225.585)	3	(0.2 estimated)	7.39	**Fe1 Ni W**
V	310.230	2	0.03000	1.21	**Be Zr W**
W	239.709	3	0.041 (ID-213) 0.04600 (ID-125G)	2.56	**Co Mo Fe1 Be Zr** Ni Ti
Zn	213.856	3	0.00400	0.181	
Zr	343.823	1	0.01800	1.95	

* See Section 1.2. for a discussion of the use of higher-order diffraction lines.

† With the exception of the Fe channels (Fe1 and Fe2), the symbols used in the Channel and Interferences columns above are interchangeable with the elements having the same symbol. The Fe1 channel was used to monitor the Fe concentration in the samples, because it generally provides more accurate corrections in the concentration range expected in air samples. The Fe2 channel is an alternate, less sensitive, channel that may be used at high Fe concentrations to assist in determining appropriate dilutions when the Fe1 channel is saturated. The third order osmium (Os) channel at 225.585 nm was the channel used to monitor the Ti concentration (see discussion in Section 1.5.2) Titanium was evaluated as a possible interference because it is common in industrial operations where W and Co are found; Osmium was not evaluated as an interference because it is an exceedingly rare element.

4.4 Determination of Qualitative and Quantitative Detection Limits and Background Equivalent Concentrations (5.7):

A modification of the International Union of Pure and Applied Chemistry (IUPAC) qualitative detection limit equation (5.16) was used for this study. According to the IUPAC convention, 3 × SD defines the qualitative detection limit; however, ICP-AES manufacturers (including ARL) generally use 2 × SD in their software.

Procedure:

The instrument was calibrated for W, Co, and the screening elements. BECs were calculated from the calibration information. The detection limits for W and Co were measured during the validation. Detection limit estimates for screened elements were obtained from reference 5.7. Reagent blanks and calibration standards of 100 µg/mL W and 10 µg/mL Co were aspirated to obtain the slope of the calibration curve. The reagent blank was measured ten times at the W and Co wavelengths to determine the SDs of the measurements. The ARL software (5.13.) was used to perform these calculations. Each DL was calculated as follows:

$$m = (I_{std} - I_{rblank}) / C_{std}$$

Qualitative DL = 2 × SD_{rblank} / m

Quantitative DL = 10 × SD_{rblank} / m

where:
SD_{rblank} = standard deviation of the reagent blank signal
I_{std} = signal intensity of the aspirated calibration standard
I_{rblank} = signal intensity of the aspirated reagent blank
C_{std} = concentration of the aspirated standard
m = slope of the calibration curve

Note: Some ICP-AES users and manufacturers prefer to use BECs to estimate DLs. The BEC is defined as the concentration of an analyte that is equal to the net intensity of the background signal for that analyte:

$$BEC = I_{rblank} / m$$

According to this latter approach, the DL is estimated to be a small fraction, e.g., 2%, of the BEC.

Results:

The results for qualitative and quantitative detection limits are shown in terms of solution and exposure concentrations in Tables 1 (in Sections 1.4.2) and 2 (in Section 1.4.3). Qualitative DLs as well as BECs for Co, W, and all the screening elements are shown in Table 16 (Section 4.3) in terms of solution concentration. The DLs averaged 2% of the corresponding BECs with a range of 0.5% to 3%.

4.5   Determination of Analytical Method Precision and Accuracy for Insoluble W:

Tungsten carbide composites with Co binder were the most representative of previous analyses requested at the OSHA Salt Lake Technical Center and they also presented the most severe test of this analytical method. Tungsten carbide and many other tungsten compounds are very dense. The pure tungsten carbides WC and W_2C have densities of 15.63 and 17.15 respectively (5.9). At 19.3 g/mL, the density of W is too high to obtain stable aerosols above 5 μm diameter (5.2). The commercially available reference materials for these composites exceed 5 μm. For this validation the materials were not sieved because they may not be sufficiently homogeneous for sieved material to match the certified composition. In addition, larger particles are generally less easily digested because they offer a small surface-to-mass ratio. The use of the unsieved matrix therefore, posed a more accurate and more difficult test for recovery determinations than could be obtained using either aerosols or sieved powders of these materials.

Procedure

Three spiked samples of each of the two most difficult insoluble matrices, 94% WC/6% Co and 88% W_2C/12% Co, (certified materials described in Section 4.1) were prepared by spiking tared 0.8-μm pore size, 37-mm diameter MCE filters that had reached constant weight in a controlled low humidity lab environment (33 - 36% RH). These were prepared at three levels representing W exposures at 0.5 ×, 1 ×, and 2 × TWA PEL for W.

Six spiked MCE filter samples representing concentrations of insoluble W near the STEL were made from pure W in order to avoid problems associated with small sample weight and the inhomogeneity in the tungsten carbide matrices. All the reagents and certified materials used for spiking were independent of the stock standards used to prepare calibration standards.

Results

The theoretical amounts of W in all insoluble analyte spikes were calculated from assay information provided by the chemical manufacturer. The analytical method precision and accuracy for insoluble W are shown in Tables 17 and 18.

Table 17

Analysis - Insoluble W TWA Determination Tungsten Carbide Matrices * (2 L/min, 4 h, 480 L, 50-mL solution volume)					
OSHA-PEL Level	N †	Mean F/T	Std Dev	CV	OE (%)
0.5 ×	6	1.0190	0.0160	0.0157	± 5.04
1 ×	6	1.0248	0.0139	0.0135	± 5.18
2 ×	6	0.9935	0.0744	0.0748	± 15.61 ‡
Summary	18	1.0124	NA	0.0448	± 10.2

F/T = Found/Theoretical   OE = Overall error (±%)
* Composition of certified materials:
87.87 for W in 94% WC
84.08 for W in 88% W_2C
† At each exposure level, three 94% WC and three 88% W_2C spiked samples were analyzed.
‡ One of the 94% WC samples at 2 × PEL gave a recovery of 0.854 and was not deleted in the statistical analysis. Reanalysis of this sample also gave a low recovery (F/T = 0.841). This was not an outlier by the Grubb's test (99% confidence level). Nothing unusual was observed in the analysis of the Co content of this sample. Variation was probably due to the inhomogeneity of the WC/Co composite.

Table 18

Analysis - Insoluble W STEL Determination Pure Tungsten Matrix * (2 L/min, 15 min, 30 L, 50-mL solution volume)					
OSHA-STEL Level	N	Mean F/T	Std Dev	CV	OE (%)
1 ×	6	1.0467	0.0212	0.0202	± 8.71

F/T = Found/Theoretical OE = Overall error (±%)
* The composition indicated on reagent certification is 100.00% W.

4.6 Determination of Analytical Method Precision and Accuracy for Soluble W:

Cobalt is not commonly present when sampling for soluble W, so it was not included in this experiment.

Procedure

Analyte spikes of W were prepared from reagents independent of calibration standards. Spikes of soluble W were made by delivery of solutions of known concentration using pipettes and micropipettes.

The 0.8-µm pore size, 37-mm diameter, MCE filters were placed in Phillips beakers and spiked at levels representing 0.5 ×, 1 ×, and 2 × TWA PEL using respectively 240, 480, and 960 µL aliquots of a 1,000 µg/mL W solution (178.72 mg of 100.4% $Na_2WO_4 \cdot 2H_2O$ diluted to 100 mL with DI H_2O). The MCE filters spiked at the STEL used 900 µL aliquots of a 100 µg/mL W solution prepared by a 1:10 dilution of the 1,000 µg/mL W solution. The gravimetric factor of 0.5596 was calculated from (100.4%/100%) × (183.85 g W)/(329.86 g $Na_2WO_4 \cdot 2H_2O$) based on reagent label analysis and formula weights. The samples were air dried prior to digestion. The samples were then diluted to 50 mL, and analyzed according to the method.

Results

The analytical method precision and accuracy data for soluble W are shown in Tables 19 and 20:

Table 19

Analysis - Soluble W TWA Determination Sodium Tungstate Dihydrate Matrix (2 L/min, 4 h, 480 L, 50-mL solution volume)					
OSHA-PEL Level	N	Mean F/T	Std Dev	CV	OE (%)
0.5 ×	6	1.0892	0.0100	0.0092	± 10.76
1 ×	6	1.0652	0.0087	0.0082	± 8.16
2 ×	6	1.0640	0.0121	0.0114	± 8.68
Summary	18	1.0728	NA	0.0097	± 9.22

F/T = Found/Theoretical OE = Overall error (±%)

Table 20

Analysis - Soluble W STEL Determination Sodium Tungstate Dihydrate Matrix (2 L/min, 15 min, 30 L, 50-mL solution volume)					
OSHA-STEL Level	N	Mean F/T	Std Dev	CV	OE (%)
1 ×	6	1.0615	0.0074	0.0070	± 7.55

F/T = Found/Theoretical OE = Overall error (±%)

4.7   Determination of Analytical Method Precision and Accuracy for Co:

Procedure

The 0.8-μm pore size, 37-mm diameter, MCE filters for this experiment were placed in Phillips beakers and spiked at levels representing Co exposures at 0.5 ×, 1 ×, and 2 × TWA PEL using 120-, 240-, and 480-μL aliquots of a 100 μg/mL Co solution respectively. To match expected matrix conditions where spectral interferences from W may be significant, these samples were also spiked with 0.5-mL aliquots of 10,000 μg/mL W (1.79 g of 100.4% $Na_2WO_4 \cdot 2H_2O$ diluted to 100 mL with DI H_2O). The W reagent and calibration standards were independent sources of W. The spiked filters in the Phillips beakers were then air dried prior to digestion. The samples were digested, diluted to 50 mL, and analyzed according to the method.

Note: The 100 μg/mL Co spiking solution was a 1:10 dilution made from a different bottle of atomic spectral standard than was used to make the two Co calibration standards. Because both bottles had the same lot number, this experiment did not provide a completely independent measure of Co recovery but did provide an adequate measure of precision. When new ICP calibration standards are prepared at SLTC, a quality assurance check is made by analyzing and comparing the old and new calibration standards. This Co ICP stock standard has checked out fine on this quality assurance test and on subsequent quality control tests using independent Co sources. A fully independent test of Co recovery is provided by the additional Co recovery experiments performed in Section 4.8.

After preparation, the resulting final solution matrix was 100 μg/mL W and would represent exposures to soluble W at 10 × TWA PEL or exposures to insoluble W at 2 × TWA PEL.

Results

Analytical method data and precision and accuracy for Co are shown below in Table 21.   The analytical method data, precision, and accuracy for 100 μg/mL W matrix is provided below Table 21:

Table 21

Analysis - Co TWA Determination (In 100 µg/mL W Solution Matrix) * (2 L/min, 480 L, 50-mL solution volume)					
OSHA-PEL Level	N	Mean F/T	Std Dev	CV	OE (%)
0.5 ×	6	1.0627	0.0484	0.0456	± 15.39 †
1 ×	6	1.0440	0.0014	0.0014	± 4.68
2 ×	6	1.0328	0.0063	0.0061	± 4.50
Summary	18	1.0465	NA	0.0266	± 9.97

F/T = Found/Theoretical OE = Overall error (±%)
* Analysis for W (100 µg/mL) matrix:
Bias = + 0.0411
CV (Pooled) = 0.0079
Overall Error (Total) = ± 5.69%
† One of the samples at 0.5 × PEL was overlooked on the day all the other samples were analyzed; it was analyzed two days later at the first opportunity. The result was not an outlier according to Grubb's test (99% confidence level).

4.8   Determination of Analytical Method Precision and Accuracy for Co at Higher Levels:
The spiked MCE filter samples of the cemented tungsten carbide matrices prepared in Section 4.5. also contained substantial amounts of Co (3.2 ×, 6.5 ×, 7.4 ×, 12.3 ×, 14.9 ×, and 28.0 × TWA PEL). These samples were also analyzed for Co. This supplementary experiment serves two purposes:

1)   To provide an independent test of Co recovery not provided in Section 4.7.
2)   To extend the validation to include levels of Co potentially found in sampling for W in cemented tungsten carbide operations.

Procedure

As described in Section 4.5, analyte spikes were prepared from certified sources independent of calibration standards. The amounts of W and Co in all insoluble analyte spikes were calculated from assay information provided by the chemical manufacturer. The weights of the spikes of the cemented tungsten carbide matrices were determined by weighing on tared 0.8-µm pore size, 37-mm diameter, MCE filters that had reached constant weight in a controlled low humidity lab environment (33 - 36% RH). The spikes filters were transferred to Phillips beakers, digested, diluted to 50 mL, and analyzed according to the method.

Results

This experiment gave an average Co recovery of 1.028 which compares well to the average Co recovery of 1.046 obtained in Section 4.7. The Co results are listed in Table 22:

Table 22

Analysis - Co TWA Determinations Above Usual Validation Range (In Insoluble Tungsten Carbide Samples at 0.5, 1, and 2 × W PEL)* (2 L/min, 4 h, 480 L, 50-mL solution volume)					
OSHA-PEL Level †	Matrix	Mean F/T	Std Dev	CV	OE (%)
3.2 ×	Co in 94% WC	1.0653	0.0190	0.0179	± 10.11
6.5 ×	Co in 94% WC	1.0663	0.0083	0.0078	± 8.19
7.4 ×	Co in 88% W_2C	1.0067	0.0099	0.0098	± 2.63
12.3 ×	Co in 94% WC	1.0330	0.0380	0.0368	± 10.66
14.9 ×	Co in 88% W_2C	0.9997	0.0101	0.0101	± 2.05
28.0 ×	Co in 88% W_2C	1.0000	0.0056	0.0056	± 1.12

Summary	18 samples (Pooled)	1.0285	NA	0.0181 (df=12)	± 6.47
	18 samples (Combined)	1.0285	NA	0.0325 (df=17)	± 9.35

F/T = Found/Theoretical   OE = Overall error (±%) df = degrees of freedom

* Composition of the certified materials: 5.45% Co in 94% WC, 11.70% Co in 88% W_2C

† N = 3 samples for each OSHA-PEL Level tested.

4.9   Assessment of Typical Levels of Blank Contamination, Analyte Carry-over, and Noise:

Typical blank contamination, carry-over, and noise between samples was surveyed by analyzing blanks interspersed with samples.

Procedure

Four blanks were prepared from the same lot of 0.8-µm pore size, 37-mm diameter, MCE filters used to prepare the spiked samples. These were subjected to the same digestion steps as the spiked samples and were analyzed along with the spiked samples described in Sections 4.5 to 4.8. All four blanks were used to evaluate contaminant levels in the sampling medium. Some of these were also analyzed after high samples and standards in order to evaluate carry-over. Carry-over can result from physical carry-over of solution between analyses. Additionally, carry-over of electronic origin can result after PMTs or other sensitive electronic components are stressed by strong signals; it may take additional time for certain channels to settle down to the same noise level measured during calibration, and the resulting excursions in electronic noise can be incorrectly interpreted as signals.

All results were calculated from concentration-response curves, corrected for reagent blank, and corrected for the interelement interferences identified in Section 4.3.

Results

Table 23 shows the blank contamination levels (µg/mL) observed:

Table 23

Element	N, µg/mL*	Element	N, µg/mL	Element	N, µg/mL	Element	N, µg/mL
Al	2, 0.12	Cr	1, 0.020	Ni	ND	Te	1, 0.080
As	ND	Cu	ND	Pb	ND	Ti	ND
Be	ND	Fe	ND	Sb	ND	V	ND
Ca	4, 0.018	Mg	2, 0.11	Se	2, 0.064	W	2, 0.070
Cd	ND	Mn	ND	Si	4, 3.3	Zn	ND
Co	4, 0.015	Mo	ND	Sn	1, 0.020	Zr	2, 0.020

* The levels of contamination are reported in the following format: number detected, mean of detected. ND indicates all four blanks were non-detected. Blank analyses above excluded replicate checks used to test for carry-over.

Carry-over and noise were observed during the validation. The worst instances are listed in Table 24:

Table 24

Preceding Sample Element(s)	Apparent Carry-Over of Element
2 µg/mL Cr,Mo,Ni,Sb,V 20 µg/mL Fe *	0.075 µg/mL As
"	0.020 µg/mL Co
"	0.13 µg/mL Mg
"	0.079 µg/mL Sb
"	0.21 µg/mL Se
"	0.080 µg/mL Sn
"	0.12 µg/mL Te
99.26 µg/mL W, 6.156 µg/mL Co	0.18 µg/mL W

* Carry-over, noise, or interferences on As, Co, Se, Sn, Te, and W were also observed when this standard was analyzed. This standard was preceded by six 2 × PEL Co samples (0.96 µg/mL Co containing 100 µg/mL W). Undercorrected As, Mg, Se, Sn, and Te interferences were also noted during the analyses of several of these 2 × PEL Co samples.

The long delay in re-achieving normal background noise levels indicates that the type of carry-over noise observed in these experiments probably arises from electronic origin. The potential for background contamination and carry-over demonstrates the need for blank analyses. This will correct for sampling media contamination and provide a quality assurance check for possible carry-over effects, faltering electronic circuits, or noisy channels. Carry-over can be diminished by lengthening the amount of time between analysis of each sample or standard. When using the parameters described in this method, the time between samples was approximately 85 seconds to change sample and 30 seconds pre-integration time to allow sample entry into the plasma.

4.10 Summary:

The validation results indicate the method meets both the NIOSH and OSHA criteria for accuracy and precision (5.5, 5.17). The results are within an acceptable range (OE < ±25%). Detection limits are adequate when samples are taken for TWA determinations for 480 min at 2 L/min, or for 15-min STEL determinations. The method is adequate for monitoring TWA, STEL, and indoor air types of exposures.

5. References

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