

Analysis of Trace Elements in Tungsten Metal using the Prodigy DC Arc

Introduction

Tungsten is a brittle, high density gray-white metal with good electrical conductivity properties and a melting point higher than all other pure metals. With the exception of carbon, tungsten has the highest melting point of all the elements in the periodic table. The electrical conductivity and thermal properties of tungsten make it suitable for use in many applications, both in its pure metallic form and as a component in an alloyed metal.

In its non-alloyed form, tungsten is used to make electrodes for arc welding, filaments for light bulbs and high performance auto parts. It also finds use in numerous electrical, spacecraft and high temperature applications. As an alloyed metal, tungsten increases the hardness and tensile strength of materials for use in wear-resistant tools, x-ray tubes, superalloys and industrial catalysts.

The analysis of trace elements in high purity tungsten is challenging using techniques that require sample digestion prior to analysis. Digestion procedures are often complex, time-consuming and increase the risk of sample contamination during preparation. DC Arc allows tungsten samples to be analyzed in their solid metallic form, eliminating the need for sample dissolution and greatly increasing the speed with which samples are prepared and analyzed. Direct analysis also eliminates sample dilution, resulting in better detection limits than those obtained with other analytical techniques.

This application note contains data to demonstrate the ability of the Teledyne Leeman Labs Prodigy DC Arc spectrometer to determine trace elements in high purity tungsten metal. The Prodigy provides high sensitivity and dispersion which, combined with appropriately chosen wavelengths and background correction points, can be used to provide accurate and reliable results for a large suite of elements in tungsten.

Experimental

Instrumentation

A **Prodigy DC Arc** Spectrometer was used to generate the data for this application note. The **Prodigy DC Arc** is a compact, bench-top simultaneous instrument featuring an 800 mm focal length Echelle optical system and a mega-pixel Large Format Programmable Array Detector (L-PAD). At 28 mm², the active area of the L-PAD is significantly larger than that of all other solid-state detectors currently used in DC Arc spectrometers.

The long focal length, combined with the large array detector, create a solid-state detection system that provides continuous wavelength coverage from 175 to 1100 nm. Well-resolved analytical signals can be measured and background corrected with a single DC Arc burn, a feature unseen in other DC Arc spectrometers with solid-state detectors. Performing data collection with a single DC Arc burn significantly reduces electrode consumption and the time required for sample analysis which increases the overall productivity of the laboratory.



An additional benefit of the L-PAD is its charge injection device (CID) design which allows programmable access to each pixel in the detector array and non-destructive readout of its stored charge. These features prevent detector saturation (blooming) over a large linear working range that can cover several orders of magnitude.

The Prodigy DC Arc Spectrometer utilizes an arc stand with a solid-state, current-stabilized power supply for enhanced stability. The power supply features a dedicated microprocessor which automatically controls the current to the arc stand for the duration of the burn. The microprocessor also allows the user to create a variety of unique current programs to be recalled as needed for a variety of sample types.

The arc stand contains a Stallwood Jet that can be used with a variety of mass-flow controlled gases for the reduction of CN bands or to increase the rate of sample burn. Gases for the Stallwood Jet are controlled with the same dedicated microprocessor that controls current through the arc stand. Multiple gases can be used over the course of a single burn and each gas flow can be independently controlled.

Operating Parameters

All standards and samples were prepared for analysis by mixing each with high purity graphite such that the ratio of sample to graphite was 6:1. All mixtures were thoroughly blended with a WIG-L-BUG for a minimum of 3 minutes before hand-packing them into sample electrodes.

All samples were analyzed on the Teledyne Leeman Labs **Prodigy DC Arc**. The instrument was operated using the arc stand conditions listed in Table 1 below. Standards and samples were burned in air and all elements were integrated using individual time gates. The remaining instrument and method conditions used are listed in *Table 1*.

Table 1. DC Arc Operating Conditions

Parameter	Setting
DC Arc Stand	
Current (volatile)	Ignition at 6 amps, jump to 10 amps, hold for 60 s
Analytical Gap	2 mm
Electrodes	
Sample Electrode (graphite)	1/4" in diameter and tapered with a 50 mg sample capacity
Counter Electrode	1/8" diameter and pointed
Sample	
Sample Size	30 mg
Internal Standard	None
Integration Time	Individual time gates were used

The sample and counter electrodes were purchased from Bay Carbon Inc (Bay City, MI) and used as received. The sample electrodes used were 1/4" in diameter and tapered with a 50 mg sample capacity (part # 1068-2). The counter electrodes used for all analyses were 1/8" in diameter and pointed (part # C-1). A 2 mm analytical gap was used and the position of the electrodes was adjusted during the sample burn to maintain a distance of 2 mm between the sample and the counter electrode.

Experimental

Calibration Standards

The instrument was calibrated with several high-purity tungsten metal standards that contained the analytes of interest at 0, 1, 10, 100 and 1000 ppm. Calibration standards were prepared by serial dilution on a weight-to-weight basis from a multi-element stock standard containing 45 elements at 1.21% (MV Laboratories, Inc., Frenchtown, NJ). All standards were weighed, mixed and prepared for analysis with graphite as described above.

Wavelength Parameters

The wavelengths and background correction points used in this method are outlined in *Table 2*. Information regarding the integration time used for the analysis of each element is also listed in *Table 2*. For each analyte of interest, background correction was performed simultaneously with the peak measurement. Additionally, all pixel data are saved which allows for future data recalculation.

The DC Arc Technique for W

DC Arc is an analytical technique that allows the emission from analytes of interest to be separated in time. Once the arc is formed, the analytical cycle progresses and elemental impurities in the sample are boiled off at varying rates. Once volatilized, each impurity is excited in the arc and emits its characteristic wavelength of light, generating a unique emission profile that can be measured by the optical spectrometer. These profiles can be used for choosing integration time periods that maximize the signal to noise ratio for each analyte of interest. An example profile is shown in Figure 1. The figure is based on a time-resolved analysis (TRA) scan of a 1000 ppm multi-element standard in a tungsten matrix obtained over the course of a DC Arc burn that lasted 60 seconds. For simplicity, only 5 wavelengths were chosen for illustration.

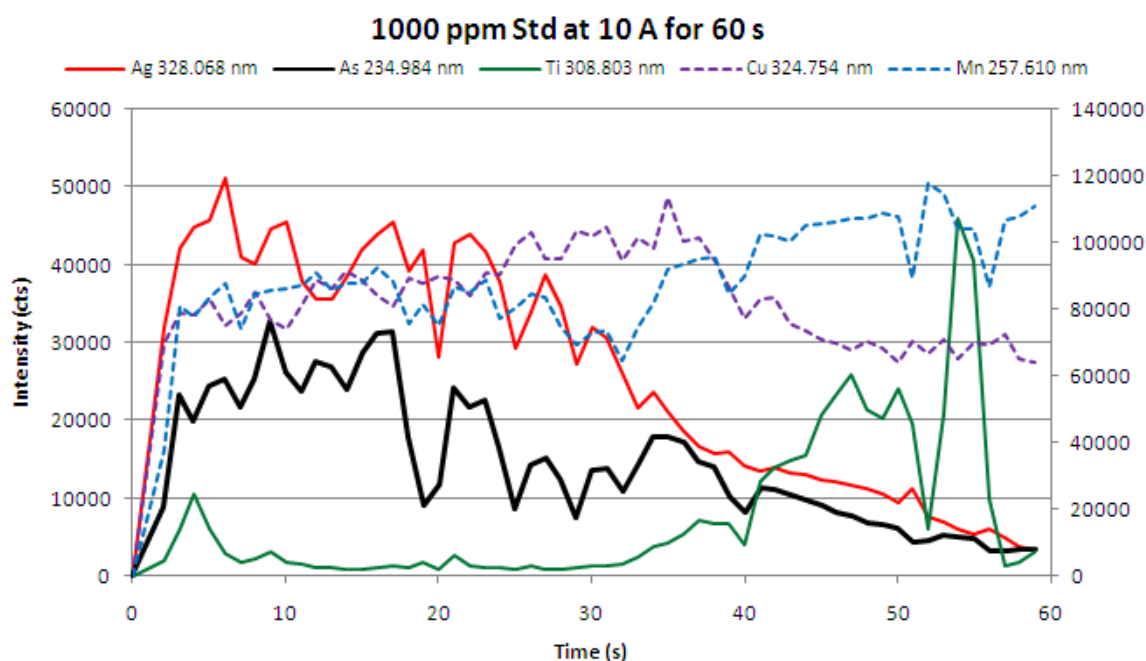


Figure 1. Time-resolved analysis scan of a multi-element standard in a W matrix.

In Figure 1, data for Ag, As and Ti is plotted on the primary axis using solid lines. Data for Cu and Mn is plotted on the secondary axis using dashed lines. Based on the data in Figure 1, appropriate time gates were chosen for all analytes of interest. Those time gates are listed in Table 2.

Element	Wavelength (nm)	Left Background Position	Right Background Position	Integration Period (s)
Ag	328.068	1	---	0-42
Al	309.271	1	---	0-48
As	234.984	---	13	0-41
B	249.773	---	15	0-30
Be	313.042	1	---	0-55
Bi	306.772	---	15	0-33
Ca	396.847	1	---	0-30
Cd	214.438	---	13	0-24.5
Co	345.351	---	15	0-42
Cr	284.984	---	13	0-53.5
Cu	324.754	1	---	0-47.5
Fe	259.940	3	---	0-42
Ga	294.364	2	---	0-53
Ge	303.906	1	---	0-42
K	766.491	---	14	0-35.5
Li	670.784	1	---	0-30
Mg	279.553	---	15	0-53.5
Mn	257.610	---	15	0-53.5
Mo	313.259	---	8	0-36.5
Na	589.592	1	---	24-55
Ni	310.155	3	---	0-51
Pb	261.418	---	15	0-37
Sb	217.589	---	15	0-51
Si	252.412	3	---	0-53
Sn	317.502	1	---	0-48
Sr	407.771	1	---	0-53
Ti	308.803	---	14	32-58
V	318.540	---	15	0-58
Zn	213.856	---	14	0-39

Table 2. Wavelengths, Background Correction Points and Integration Times Used

The Prodigy typically uses a 3 x 15 pixel subarray, centered on the wavelength of interest, to collect data for each analyte. However, subarrays can be up to 27 pixels in width and 5 pixels in height if needed. The analytical peaks and background correction points are defined in each subarray with pixel position and width values.

An example of the data collection that takes place in each subarray is illustrated graphically in *Figure 2*. This figure represents the data collected for Cu at 324.754 nm in the 1 ppm calibration standard. In *Figure 2*, the left background correction point is illustrated in blue at pixel position 1. Background correction on the right-hand side of the peak has been eliminated. The pixels used for integrating the analytical peak are illustrated in green at positions 7, 8 and 9.

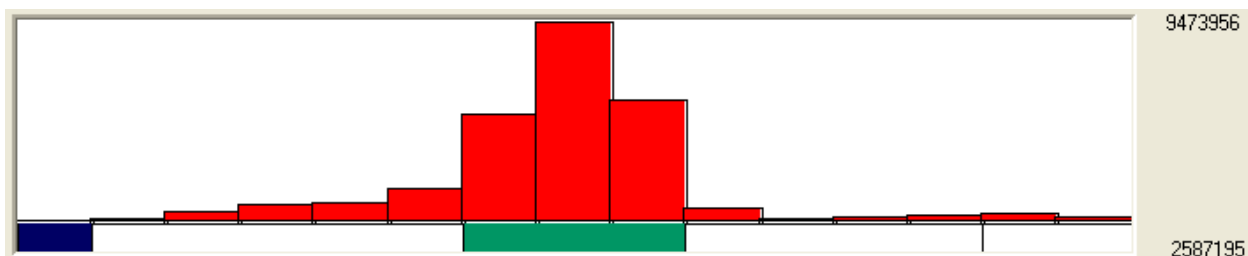


Figure 2. Graphical Representation of the Cu 324.754 nm Subarray for the 1 ppm Calibration Standard

Examples of typical calibration curves for elements measured in high purity tungsten are illustrated in Figures 3 and 4. Figures 3 and 4 contain calibration curves for Bi at 306.772 nm and Sn at 283.999 nm, respectively, to demonstrate typical precision and linearity for the analytes measured in this work.

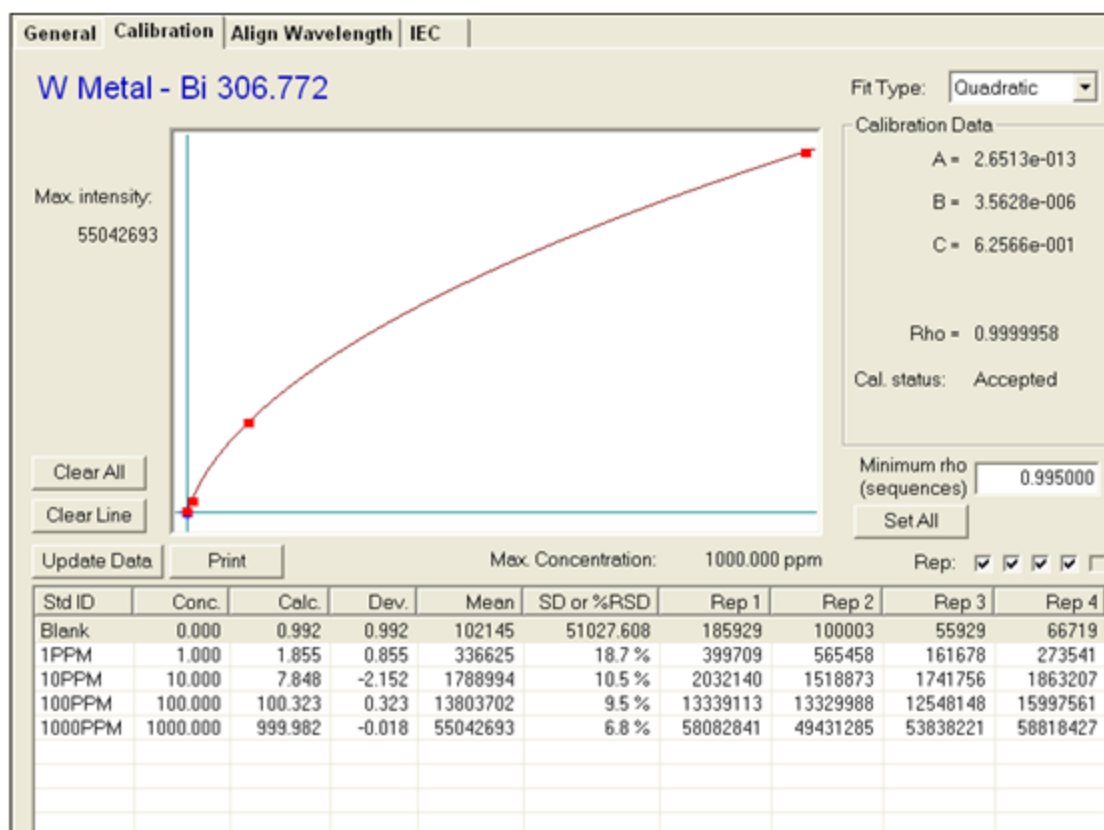


Figure 3. Calibration Curve of Bi at 306.772 nm in High Purity Tungsten

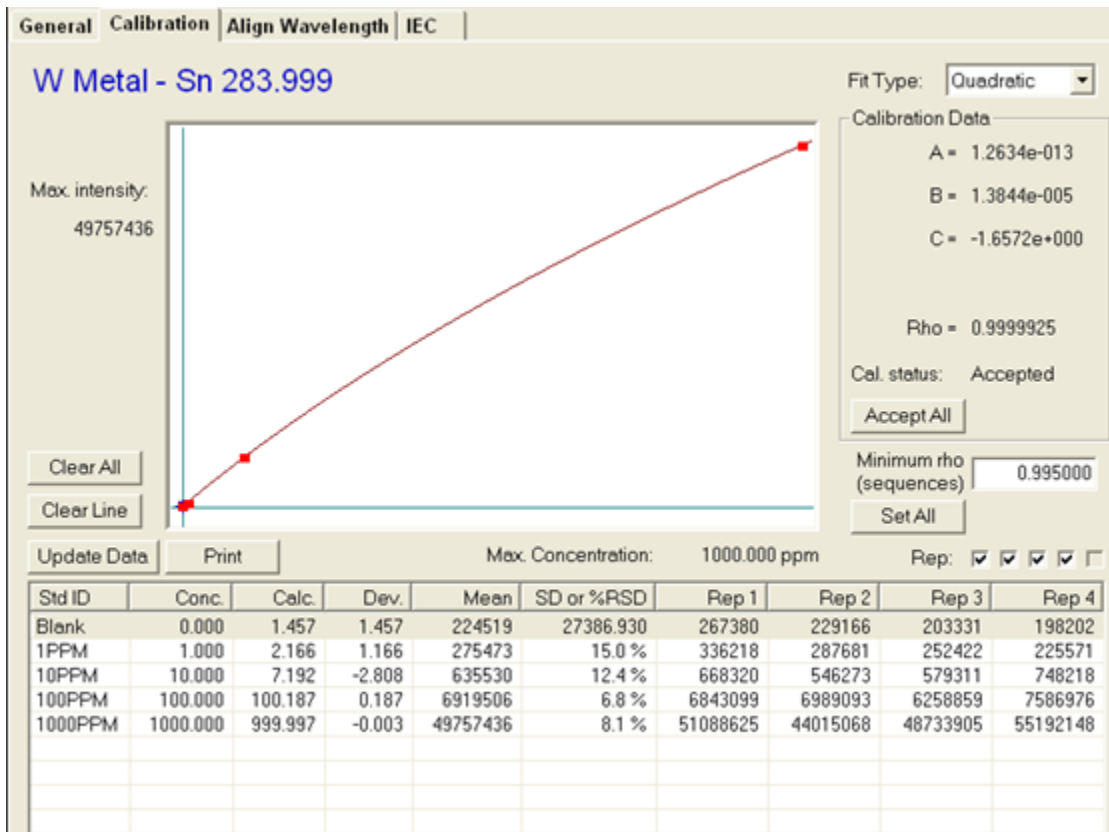


Figure 4. Calibration Curve of Sn at 283.999 nm in High Purity Tungsten

Results and Discussion

Detection Limits

A study was performed to determine the instrument's detection limits for the elements of interest. Detection limits were calculated based on 3 times the standard deviation of 7 replicate measurements of the calibration blank. Results for the detection limit study are listed in *Table 3* in units of parts per million (ppm).

Element	Wavelength (nm)	Detection Limit (ppm)
Ag	328.068	0.025
Al	309.271	0.40
As	234.984	1.2
B	249.773	0.11
Be	313.042	0.012
Bi	306.772	1.2
Ca	396.847	0.34
Cd	214.438	0.30
Co	345.351	0.54
Cr	284.984	0.25
Cu	324.754	0.063
Fe	259.940	0.95
Ga	294.364	1.0
Ge	303.906	0.14
K	766.491	0.42
Li	670.784	0.34
Mg	279.553	0.083
Mn	257.610	0.045
Mo	313.259	6.4
Na	589.592	4.3
Ni	310.155	0.096
Pb	261.418	0.51
Sb	217.589	0.47
Si	252.412	0.25
Sn	317.502	0.68
Sr	407.771	2.8
Ti	308.803	0.086
V	318.540	1.0
Zn	213.856	0.37

Conclusions

The analysis of tungsten metal using the *Prodigy DC Arc* Spectrometer demonstrates that the current-controlled DC Arc power supply, combined with the simultaneous data collection of both peak and background data, provides reproducible sample burns which is reflected in the detection limits obtained for trace elements in a tungsten metal matrix.