

Analysis of Trace Elements in Tungsten Carbide using the Teledyne Leeman Labs Prodigy DC Arc

INTRODUCTION

Tungsten carbide is a fine gray powder with a melting point of 2870°C and a hardness of 8.5-9.0, surpassed in hardness only by diamond materials. Tungsten carbide is produced via reaction between tungsten metal and carbon at high temperatures; it is not a naturally occurring compound. The hardness, melting point and electrical conductivity properties of tungsten carbide make it suitable for use in many applications;

In its powdered form, tungsten carbide can be pressed into various shapes for use in tools, abrasives, jewelry, industrial drills, armor-piercing ammunition, spikes for snowmobile equipment and studs for bicycle tires. Tungsten carbide is predominantly used in combination with metallic cobalt to produce cemented carbide (also known as tungsten-carbide cobalt). Cemented carbide is used to improve the strength, hardness and thermal stability of wear parts and mining tools which increases the lifetime and robustness of products such as industrial punches and hot rollers used for rolling steel.



The analysis of trace elements in high purity tungsten carbide 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 carbide samples to be analyzed in their solid 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* to determine trace elements in high purity tungsten carbide. 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 carbide.

Experimental

Instrument

A **Prodigy DC Arc** 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 x 28 mm, 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 over a large linear working range that can cover several orders of magnitude.

The **Prodigy DC Arc** 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 a carrier consisting of a 50:4:1 blend of graphite, sodium fluoride and germanium (IV) oxide. The standards and samples were mixed such that the ratio of standard/sample to carrier-containing graphite was 1:1. Each mixture was thoroughly blended with a SPEX mixer/mill for a minimum of 5 minutes before hand-packing it 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 for 60 seconds.

Table 1. DC Arc Operating Conditions

Parameter	Setting
DC Arc Stand	
Current	Ignition at 6A, hold for 2s, jump to 10A, hold for 58 s
Analytical Gap	4 mm
Electrodes	
Sample Electrode	3/16" diameter with an undercut cup
Counter Electrode	1/8" diameter and pointed
Sample	
Sample Size	Hand-packed, approximately 40 mg
Internal Standard	None
Integration Time	0-60 s

The sample and counter electrodes were purchased from Bay Carbon Inc (Bay City, MI) and used as received. The sample electrodes used were 3/16" in diameter with an undercut cup (part # S-15). The counter electrodes used were 1/8" in diameter and pointed (part # C-1). A 4 mm analytical gap was used and the position of the electrodes was adjusted during the sample burn to maintain a distance of 4 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, 50, 100, 500, and 5000 ppm. Tungsten metal was used for calibration instead of tungsten carbide because tungsten metal behaves similarly to tungsten carbide in a DC Arc, and tungsten metal is readily obtained at a higher purity. 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 WC

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 500 ppm multi-element standard in a tungsten matrix obtained over the course of a DC Arc burn that lasted 60 seconds.

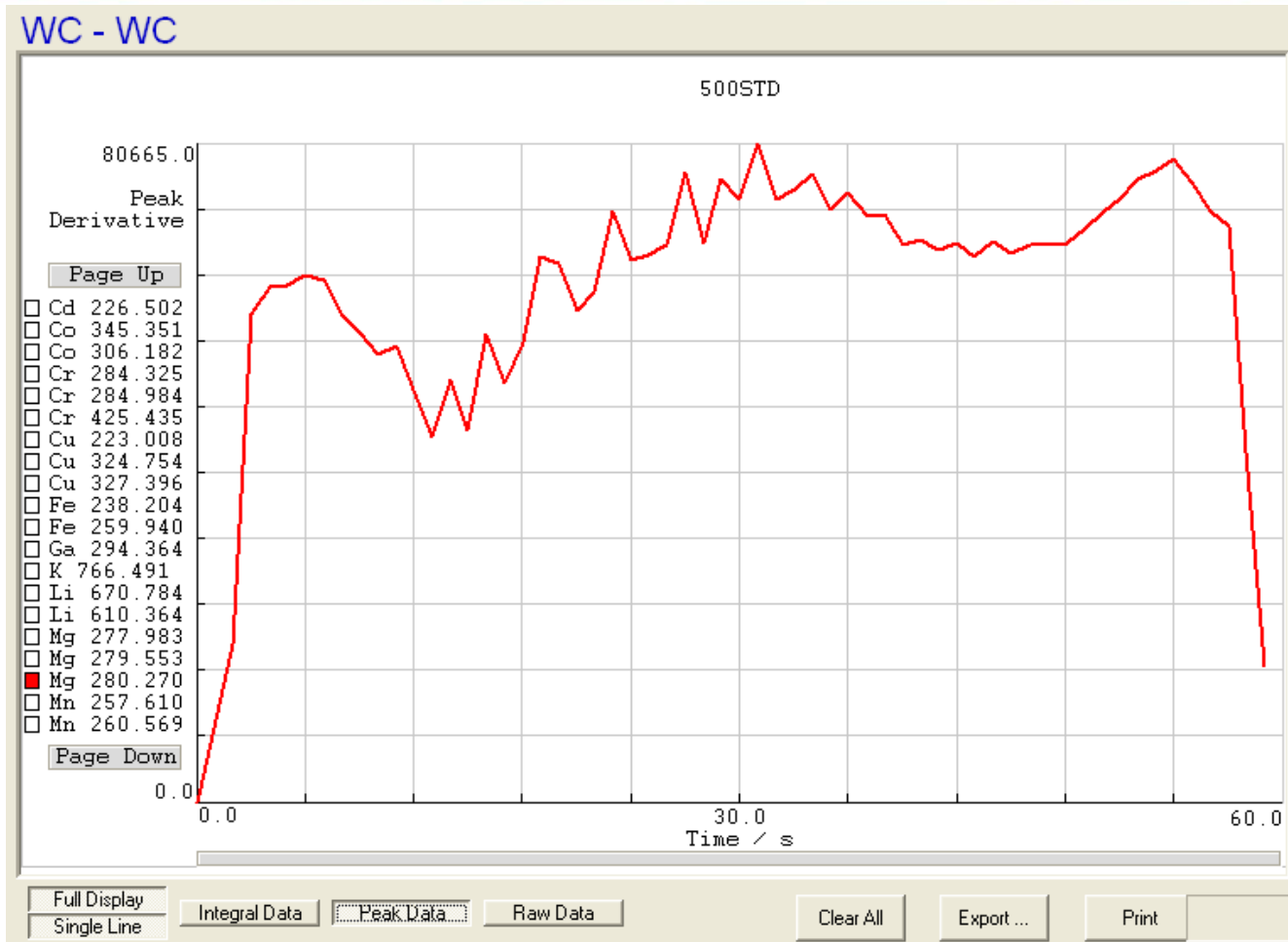


Figure 1. Time-Resolved Analysis Scan of Mg in the 500 ppm Calibration Standard

In Figure 1, data for the emission of Mg at 280 nm is plotted as a function of time. As illustrated above, significant emission from Mg was observed over the course of the entire arc burn. For this reason, emission from Mg was collected from 0-60 seconds. All wavelengths were examined in this fashion and similar emission patterns were observed. For this reason, the emission from all elements was collected from 0-60 seconds. Those time gates are listed in Table 2.

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

Element	Wavelength (nm)	Left Background Position	Right Background Position	Integration Period (s)
Ag	328.068	---	15	0-60
Al	308.216	1	---	0-60
As	193.759	---	15	0-60
B	249.773	---	15	0-60
Be	234.861	---	15	0-60
Bi	306.772	---	15	0-60
Ca	396.847	1	---	0-60
Cd	226.502	1	---	0-60
Co	345.351	---	15	0-60
Cr	284.984	---	13	0-60
Cu	324.754	1	---	0-60
Fe	238.204	---	15	0-60
Ga	294.364	1	---	0-60
K	766.491	1	15	0-60
Li	670.784	1	---	0-60
Mg	280.270	---	15	0-60
Mn	257.610	---	14	0-60
Mo	313.259	---	10	0-60
Ni	305.082	4	---	0-60
Pb	261.418	---	15	0-60
Si	252.412	3	---	0-60
Sn	317.502	1	---	0-60
Sr	407.771	1	---	0-60
Ti	308.803	---	12	0-60
V	318.54	---	11	0-60
Zn	213.856	---	15	0-60

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 Zn at 213.856 nm in the 10 ppm calibration standard. In Figure 2, the right background correction point is illustrated in blue at pixel position 15. Background correction on the left-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.

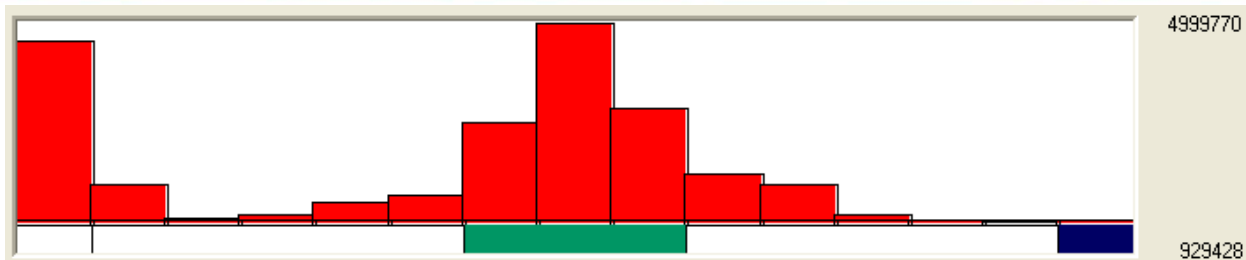


Figure 2. Graphical Representation of the Zn 213.856 nm Subarray for the 10 ppm Calibration Std

Examples of typical calibration curves for elements measured in high purity tungsten carbide are illustrated in Figures 3 and 4. Figures 3 and 4 contain calibration curves for Cd at 214.438 nm and Cr at 284.984 nm, respectively, to demonstrate typical precision and accuracy for the analytes measured in this work.

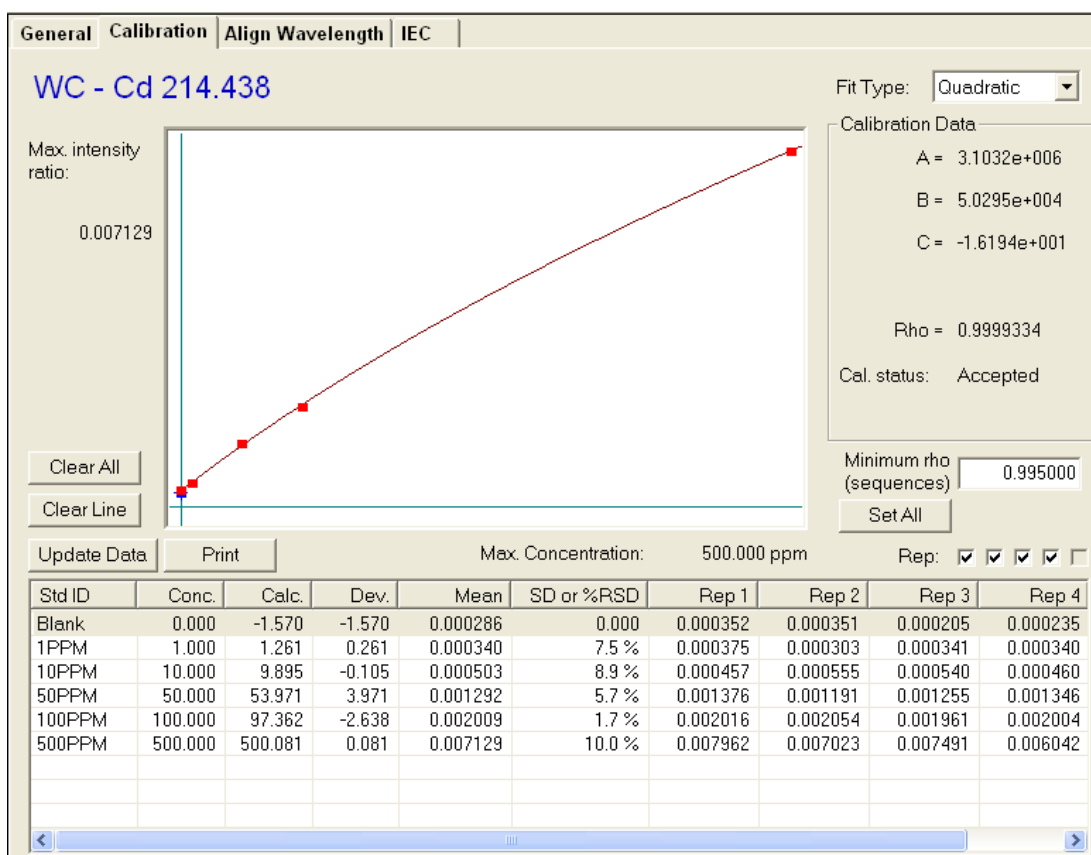


Figure 3. Calibration Curve of Cd at 214.438 nm in High Purity Tungsten Carbide

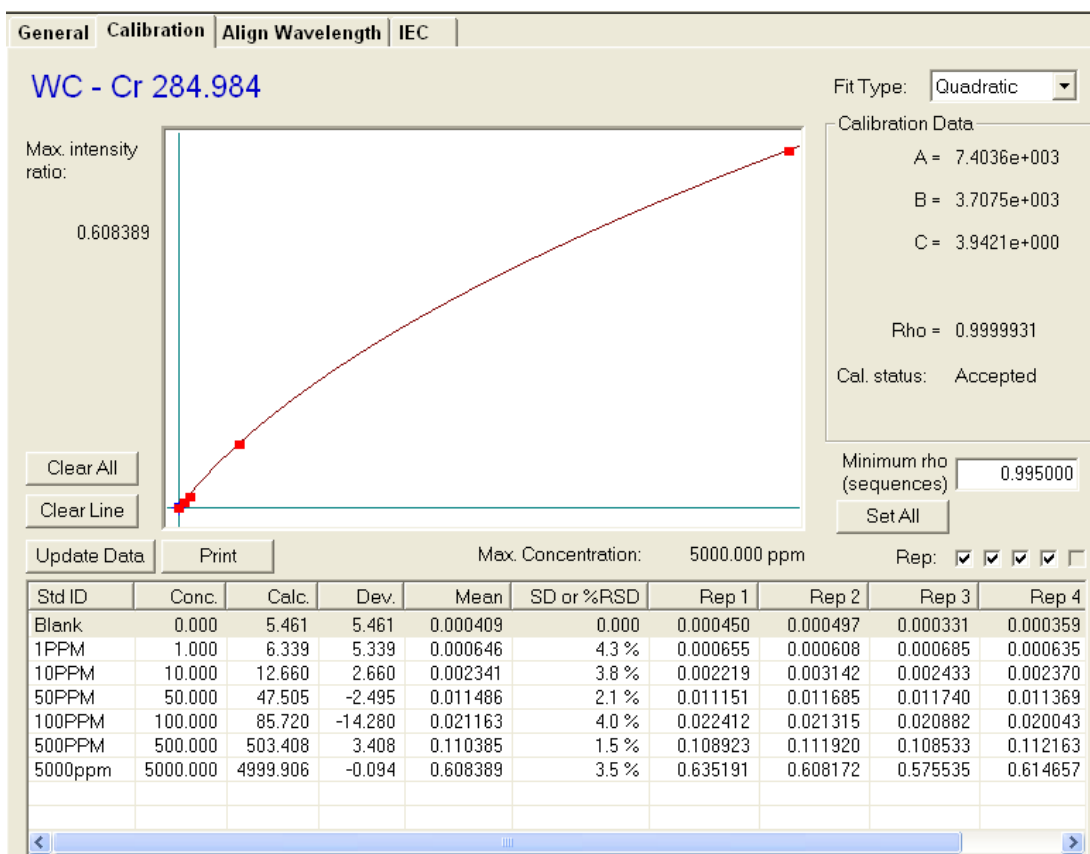


Figure 4. Calibration Curve of Cr at 284.984 nm in High Purity Tungsten Carbide

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 8 replicate measurements of the calibration blank. Results for the detection limit study are listed in Table 3 in units of parts per million (ppm). Since sodium fluoride and germanium (IV) oxide were used in the sample preparation method, detection limits for Na and Ge were not calculated.

The sodium fluoride material used in this work contained several impurities such as Al, Cd, Fe and Mg. These impurities were at relatively high concentrations which degraded the detection limits that otherwise would have been obtained in a pure tungsten carbide matrix. It should also be noted that the detection limit for Si reflects inhomogenities in the standards more than imprecision in the instrument.

Table 3. Detection Limits in High Purity Tungsten Carbide

Element	Wavelength (nm)	Detection Limit (ppm)
Ag	328.068	0.014
Al*	308.216	3.8
As	193.759	6.6
B	249.773	0.80
Be	234.861	0.030
Bi	306.772	0.16
Ca	396.847	0.56
Cd*	226.502	4.5
Co	345.351	0.19
Cr	284.984	0.55
Cu	324.754	0.17
Fe*	238.204	2.3
Ga	294.364	0.080
K	766.491	0.59
Li	670.784	0.016
Mg*	280.270	1.2
Mn	257.610	0.88
Mo	313.259	2.8
Ni	305.082	0.23
Pb	261.418	0.26
Si	252.412	5.4
Sn	317.502	0.14
Sr	407.771	0.08
Ti	308.803	0.11
V	318.54	0.20
Zn	213.856	0.10

*Detection limits for Al, Cd, Fe and Mg were degraded due to contaminants in the NaF carrier used

Conclusion

The analysis of tungsten carbide using the *Prodigy DC Arc* 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 carbide matrix.