



# Analysis of Trace Elements in Molybdenum Metal using the Teledyne Leeman Labs Prodigy DC Arc

## Introduction

Metallic molybdenum is a silver gray metal that melts at 2623 °C, the sixth highest melting point of all elements in the periodic table. It readily forms carbide compounds that are both strong and stable, and forms volatile oxide compounds when heated above 600 °C in atmosphere. The strength and mechanical stability of molybdenum at temperatures reaching to 1900 °C make it suitable for use in many applications, both in its pure metallic form and as a component in an alloyed metal.

As a pure metal, molybdenum is used in light bulb filaments, high temperature furnace parts, and scratch-resistant mirrors and optics. In its alloyed form, molybdenum is primarily used in the production of stainless steels and in alloy steels. These materials are used to construct low-friction, wear-resistant automotive parts, gas transmission pipes, cast irons, industrial catalysts, smoke and flame retardants and gas turbine parts.

The analysis of trace elements in high purity molybdenum 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 molybdenum 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 molybdenum 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 molybdenum.

## Experimental

### Instrument

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 mm<sup>2</sup>, 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** 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 analyzed in their native form without the addition of graphite or a powdered internal standard. All analyses were performed on the Teledyne Leeman Labs **Prodigy DC Arc**. For all analyses, the Stallwood Jet was used with a 70:30 mixture of Ar:O<sub>2</sub> such that the total gas flow through the jet was 2.5 L/min. All elements were integrated using individual time gates and the remaining instrument and method conditions used are listed in Table 1.

*Table 1. DC Arc Operating Conditions*

Parameter	Setting
<b>DC Arc Stand</b>	
Current	Ignition at 9.5 amps, hold for 90 s
Analytical Gap	4 mm
<b>Electrodes</b>	
Sample Electrode (graphite)	1/4" in diameter and tapered with a 50 mg sample capacity
Counter Electrode	1/8" diameter and pointed
<b>Sample</b>	
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 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**

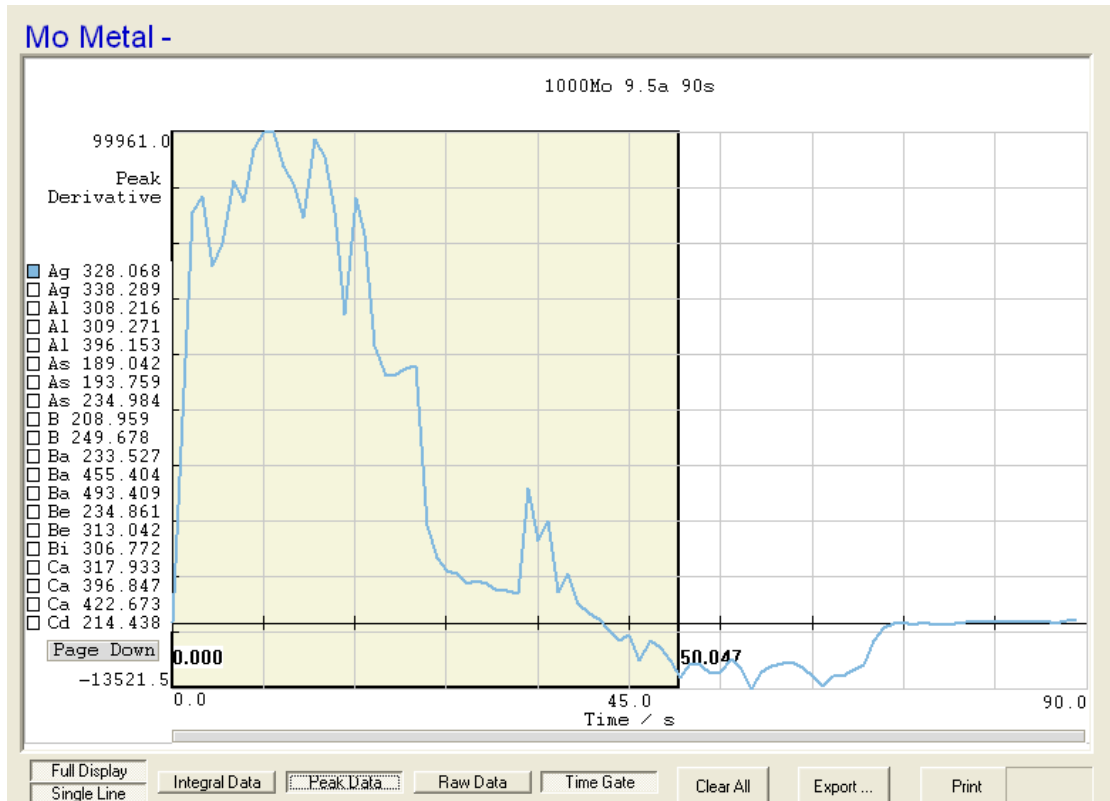
The instrument was calibrated with several high-purity molybdenum powdered metal standards that contained the analytes of interest at 0, 1, 10, 100 and 1000 ppm. Calibration standards were prepared by serial dilution on a weight-to-weight basis from a multi-element stock standard containing each of 45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

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 molybdenum metal matrix obtained over the course of a DC Arc burn that lasted 90 seconds.



**Figure 1.** Time-Resolved Analysis Scan of Ag in the 1000 ppm Calibration Standard

In Figure 1, data for the emission of Ag at 328 nm is plotted as a function of time. As illustrated above, the majority of the emission from Ag was observed during the first 50 seconds of the arc burn. For this reason, emission from this element was collected from 0-50 seconds. All wavelengths were examined in this fashion and suitable integration periods were chosen for each. Those time gates are listed in Table 2.

Element	Wavelength (nm)	Left Background Position	Right Background Position	Time Gates (s)
Ag	328.068	1	---	0-50
As	193.759	---	14	0-90
B	249.678	---	14	0-90
Ba	455.404	---	15	0-65
Be	234.861	1	---	0-90
Ca	396.847	4	---	0-90
Cd	226.502	2	---	0-15
Co	352.981	2	---	0-90
Cr	427.480	3	---	0-90
Cu	327.396	1	---	0-60
Fe	259.940	1	---	0-90
Ga	294.364	1	---	0-45
Ge	270.963	---	13	0-35
Mg	285.213	1	---	0-90
Mn	257.610	1	---	0-81.5
Na	588.995	---	15	0-65
Ni	305.082	---	15	0-90
P	253.565	3	---	0-83.4
Pb	283.307	---	14	0-27.4
Sb	217.589	4	---	0-72
Se	203.985	---	13	0-63.4
Si	251.612	---	15	0-90
Sn	283.999	---	14	0-45
Te	214.275	5	---	0-37
Ti	334.941	---	12	9-90
Tl	535.046	---	15	0-25
V	437.924	3	---	0-90
Zn	206.191	---	15	0-26.4
Zr	349.621	---	11	9.5-90

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

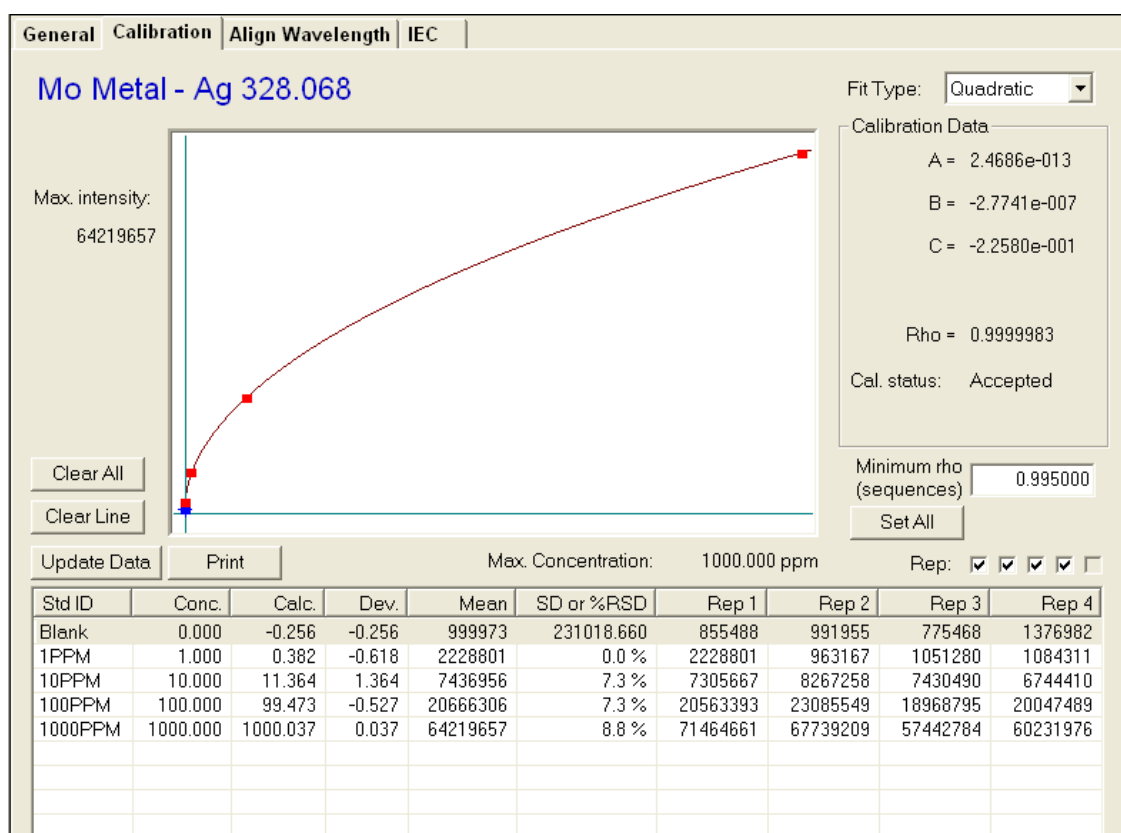
The Prodigy typically uses a 3 x 15 pixel subarray, centered on the wavelength of interest, to collect data for each analyte. However, subarrays can be up to 27 pixels in width and 5 pixels in height if needed. The analytical peaks and background correction points are defined in each subarray with pixel 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 Be at 234.861 nm in the 10 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 Be 234.861 nm Subarray for the 10 ppm Calibration Std

Examples of typical calibration curves for elements measured in high purity molybdenum are illustrated in Figures 3 and 4. Figures 3 and 4 contain calibration curves for Ag at 328.068 nm and Zn at 206.191 nm, respectively, to demonstrate typical precision and accuracy for the analytes measured in this work.



**Figure 3.** Calibration Curve of Ag at 328.068 nm in High Purity Molybdenum

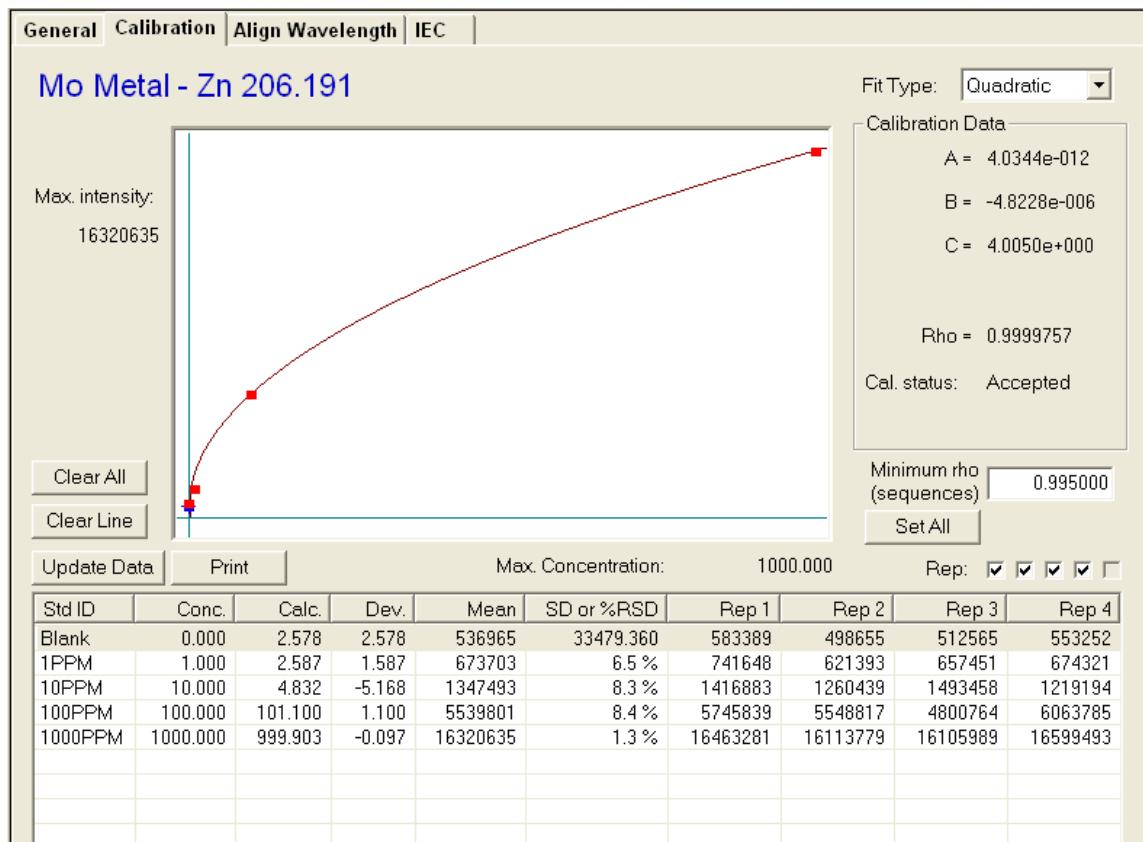


Figure 4. Calibration Curve of Zn at 206.191 nm in High Purity Molybdenum

## 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	0.14
As	193.759	2.9
B	249.678	0.54
Ba	455.404	2.8
Be	234.861	0.11
Ca	396.847	1.0
Cd	226.502	0.33
Co	352.981	4.3
Cr	427.480	3.0
Cu	327.396	0.37
Fe	259.940	1.4
Ga	294.364	1.3
Ge	270.963	4.6
Mg	285.213	0.11
Mn	257.610	0.83
Na	588.995	0.09
Ni	305.082	3.1
P	253.565	20
Pb	283.307	14
Sb	217.589	1.1
Se	203.985	4.2
Si	251.612	12
Sn	283.999	3.4
Te	214.275	2.5
Ti	334.941	1.3
Tl	535.046	3.5
V	437.924	26
Zn	206.191	0.02
Zr	349.621	4.3

*Table 3. Detection Limits in High Purity Molybdenum Metal*

## Conclusions

The analysis of molybdenum 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 molybdenum metal matrix.

Detection limits for refractory elements such as P, Pb, Si, Tl and V were higher than expected and are most likely due to insufficient and irreproducible evolution from the sample matrix. In order to avoid sample ejection, a relatively low current was used for all analyses. The low arc current prevented the metal from becoming hot enough to allow refractory elements to significantly evolve from the sample matrix. Therefore, the detection limits for those elements reflect low and irreproducible evolution more than imprecision in the instrument. Detection limits for refractory elements improve when molybdenum is analyzed in its oxide form as that matrix burns smoothly under higher current conditions (refer to application note for trace elements in molybdenum oxide).