

# Analysis of Trace Elements in Molybdenum Oxide using the Prodigy DC Arc

## Introduction

The determination of trace level impurities in molybdenum oxide is important to many industries. Molybdenum exists in several different oxidation states as part of various oxide compounds; however, molybdenum trioxide ( $\text{MoO}_3$ ) is the oxide compound most widely used and produced. Molybdenum trioxide occurs as the mineral molybdenite and is either yellow or light blue in color.

Chemical grade molybdenum oxide is often used in frits, glazes, pigments and industrial catalysts. Technical grade molybdenum oxide is most often used in the production of steels and corrosion-resistant alloys. Molybdenum oxide is also used to produce nanocrystals which are used in the production of various coatings, plastics, nanowires and electrochemical capacitors.

The analysis of trace elements in high purity molybdenum oxide 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. In contrast, DC Arc allows molybdenum oxide samples to be analyzed in their native 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 trioxide which will be referred to as molybdenum oxide in this work. 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 oxide.

## 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  $28 \text{ mm}^2$ , 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 samples were analyzed on the Teledyne Leeman Labs **Prodigy DC Arc**. The instrument was operated using the arc stand conditions listed in Table 1. Standards were burned in air and all elements were integrated using individual time gates. All instrument and method conditions used are listed in Table 1.

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

*Table 1. DC Arc Operating Conditions*

Parameter	Setting
<b>DC Arc Stand</b>	
Current	Ignite at 6A, hold at 6A for 2s; jump to 12A and hold for 30s; jump to 15A and hold for 28s
Stallwood Jet	None
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>	
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

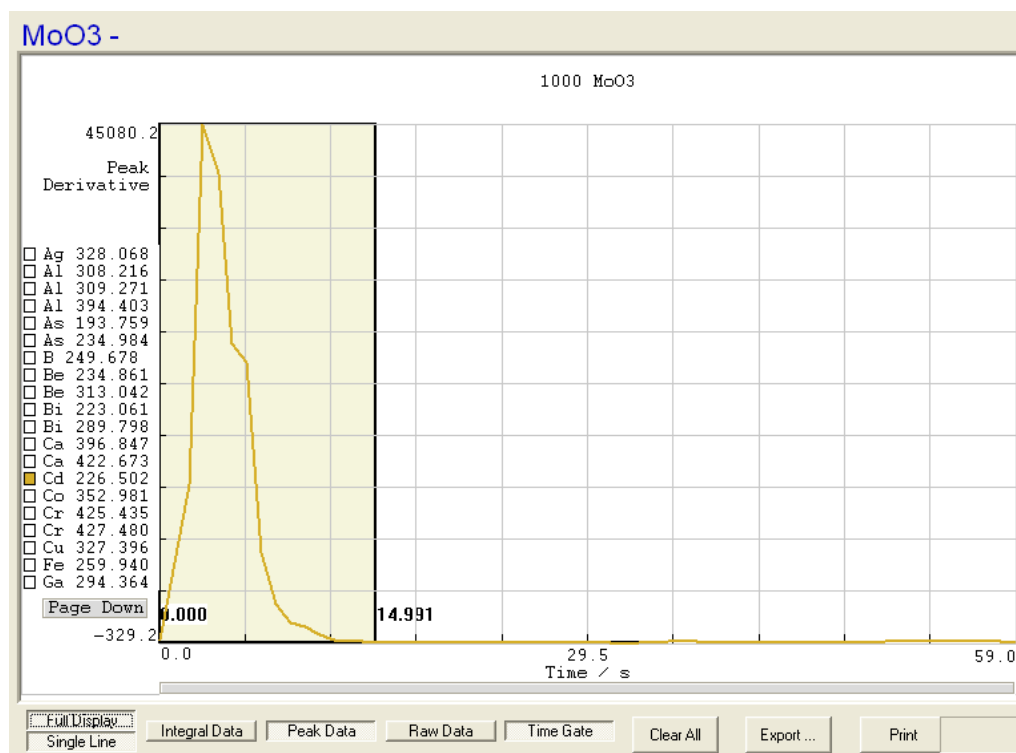
The instrument was calibrated with several high-purity molybdenum oxide standards that contained the analytes of interest at 0, 1, 10, 100 and 1000 ppm. To prepare the molybdenum oxide matrix for all calibration standards, high purity Mo metal was heated in a muffle furnace at 650 °C overnight to convert the metal to its oxide form. Calibration standards were prepared in this matrix 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

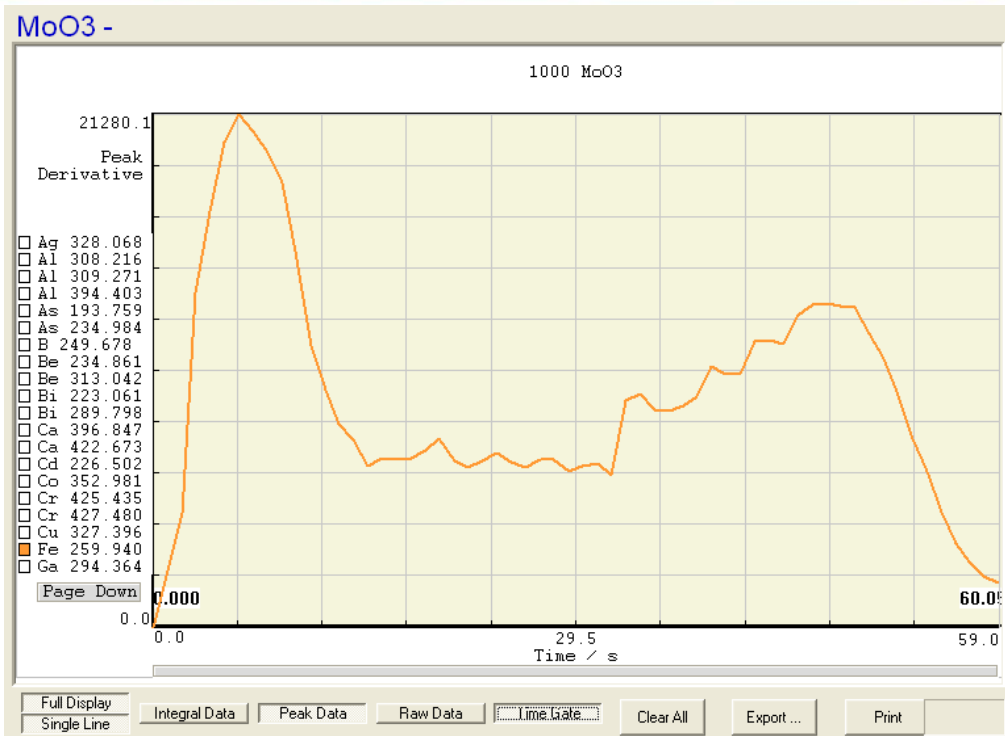
The wavelengths and background correction points used in this method are outlined in Table 2. Information regarding the integration time used for the analysis of each element is also listed in Table 2. For each analyte of interest, background correction was performed simultaneously with the peak measurement.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

## The DC Arc Technique for Mo Oxide

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. Example profiles are shown in Figures 1 and 2. The figures are based on time-resolved analysis (TRA) scans of a 1000 ppm multi-element standard in a molybdenum oxide matrix obtained over the course of a DC Arc burn that lasted 60 seconds.



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



**Figure 2.** Time-Resolved Analysis Scan of the 1000 ppm Calibration Standard

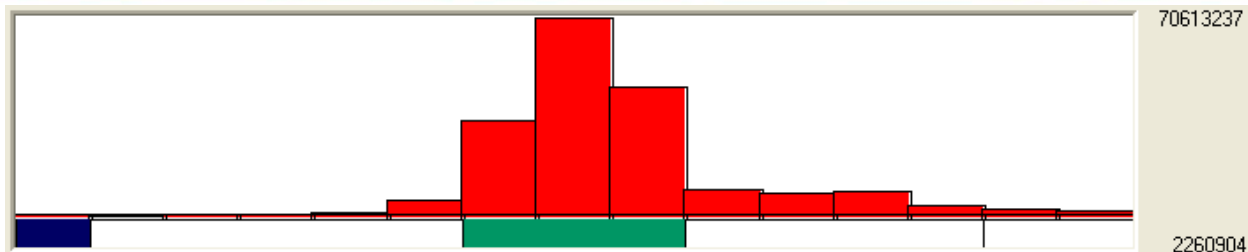
In Figures 1 and 2, data for the emission of Cd at 226 nm and Fe at 259 nm, respectively, are plotted as a function of time. As illustrated above, the majority of the emission from Cd was observed during the first 15 seconds of the arc burn while the emission for Fe was observed during the first 60 seconds of the burn with relative increases of emission toward the beginning and end of the burn. For this reason, emission from Cd and Fe was collected from 0-15 seconds and from 0-60 seconds, respectively. All wavelengths were examined in this fashion and suitable integration periods were chosen for each. Those time gates are listed in Table 2 below.

Element	Wavelength (nm)	Left Background Position	Right Background Position	Integration Time (s)
Ag	328.068	1	---	0-30.5
Al	394.403	---	11	0-45.5
As	193.759	---	13	0-60
B	249.678	---	14	0-60
Be	234.861	1	---	0-60
Bi	223.061	---	15	0-22
Ca	396.847	4	---	0-45
Cd	226.502	1	---	0-15
Co	352.981	---	15	0-60
Cr	427.480	3	---	0-60
Cu	327.396	1	---	0-46
Fe	240.488	---	15	0-60
Ga	294.364	1	---	0-30
Ge	270.963	---	13	0-30.5
K	766.491	---	15	0-25
Li	670.784	---	11	10-60
Mg	285.213	1	---	0-30
Mn	257.610	1	---	0-46
Na	588.995	---	27	0-60
Ni	305.082	---	15	0-55
P	253.565	2	---	0-31
Pb	283.307	---	15	0-21
Sb	206.833	3	---	0-30.5
Se	203.985	---	13	1-20
Si	252.412	4	---	0-55
Sn	283.999	---	14	0-30.5
Te	214.275	---	13	0-21
Ti	337.280	5	---	0-60
Ti	535.046	1	---	0-20
V	310.230	---	15	0-60
Zn	213.856	1	---	0-30
Zr	343.823	4	---	0-60

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

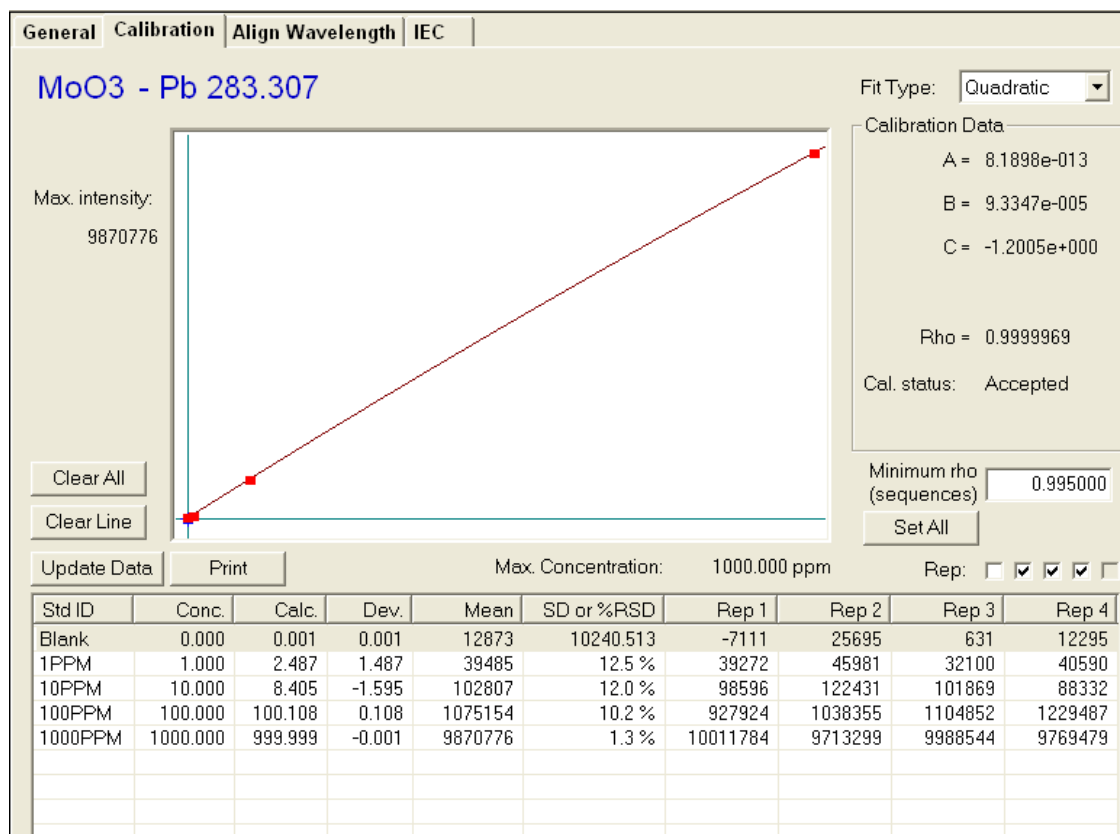
The Prodigy typically uses a 3 x 15 pixel subarray, centered on the wavelength of interest, to collect data for each analyte. However, subarrays can be up to 27 pixels in width and 5 pixels in height if needed. The analytical peaks and background correction points are defined in each subarray with pixel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

An example of the data collection that takes place in each subarray is illustrated graphically in Figure 3. This figure represents the data collected for Be at 234.861 nm in the 10 ppm calibration standard. In Figure 3, 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 3.** 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 oxide are illustrated in Figures 4 and 5. Figures 4 and 5 contain calibration curves for Pb at 283.307 nm and Sb at 206.833 nm, respectively, to demonstrate typical precision and accuracy for the analytes measured in this work.



**Figure 4.** Calibration Curve of Pb at 283.307 nm in High Purity Molybdenum Oxide

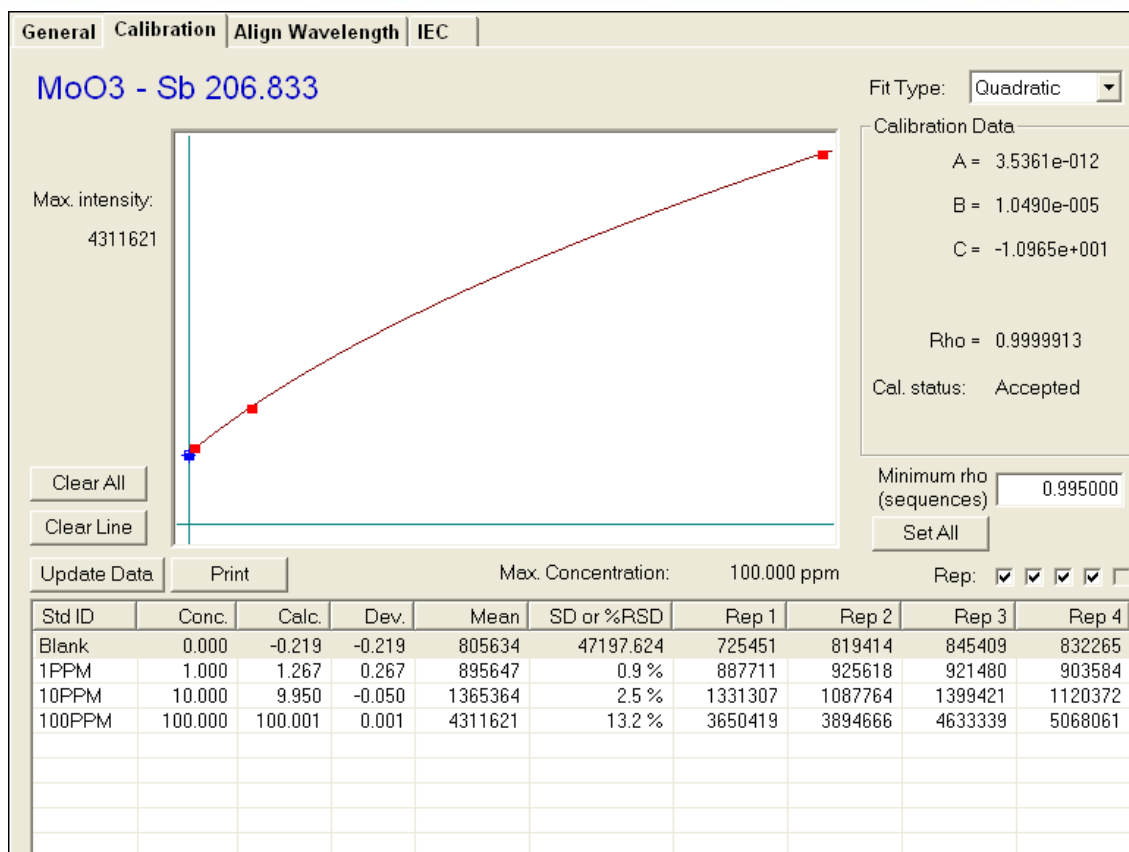


Figure 5. Calibration Curve of Sb at 206.833 nm in High Purity Molybdenum Oxide

## 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). It should be noted that the detection limit for Ca is slightly worse than expected and is presumed to be due to a combination of rogue contamination and slight inhomogeneities in the mixed standards.

Element	Wavelength (nm)	Detection Limit (ppm)
Ag	328.068	0.12
Al	394.403	6.2
As	193.759	1.9
B	249.678	1.8
Be	234.861	0.006
Bi	223.061	1.2
Ca	396.847	3.5
Cd	226.502	0.28
Co	352.981	5.0
Cr	427.480	5.7
Cu	327.396	0.31
Fe	240.488	1.2
Ga	294.364	1.3
Ge	270.963	2.8
K	766.491	4.9
Li	670.784	2.9
Mg	285.213	0.66
Mn	257.610	0.32
Na	588.995	2.0
Ni	305.082	2.1
P	253.565	3.6
Pb	283.307	4.6
Sb	206.833	0.77
Se	203.985	1.3
Si	252.412	2.6
Sn	283.999	1.8
Te	214.275	0.83
Ti	337.280	0.61
Ti	535.046	2.5
V	310.230	0.33
Zn	213.856	0.12
Zr	343.823	9.6

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

## Conclusions

The analysis of molybdenum oxide 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 oxide matrix.

As indicated in Table 3, detection limits for refractory elements such as P, Pb, Si, Ti and V improve when molybdenum is analyzed in its oxide form as compared to its metallic form (refer to application note for trace elements in molybdenum metal). This matrix tolerated higher arc currents which allowed the material to become hot enough to produce significant and reproducible emission signals from refractory elements which were challenging to analyze in a molybdenum metal matrix.