Prodigy DC Arc

Application Note: 1077

Analysis of Trace Elements in Tantalum Oxide Using the Teledyne Leeman Labs Prodigy DC Arc

INTRODUCTION

Tantalum is a blue-gray metal with a melting point of 3017ºC, the fifth highest behind tungsten, rhenium, osmium and carbon. Tantalum is found in the Earth's crust at concentrations between 1 and 2 µg g^{-1} by weight and naturally occurs in minerals such as betafite, columbite, simpsonite and tantalite. As a pure metal, tantalum is used to produce capacitors and resistors that are found in computers, DVD players, automotive electronics and portable telephones.

Due to its heat and electrical conductivity properties, along with its density and resistance to acid corrosion, tantalum is predominantly used as an alloyed metal. As an alloyed metal, tantalum is used in the production of super alloys, carbide tools, jet engine components and nuclear reactors. Since tantalum is resistant to corrosion, tantalum-based alloys are ideal for producing surgical instruments, orthopedic implants, chemical reaction vessels and heat exchanging coils that are used in chemical processing plants. In its oxide form, tantalum is used in the production of camera lenses, watches, glasses with high refractive indices, x-ray films and vacuum furnace parts.

The analysis of trace elements in high purity tantalum (in both its metallic and oxide forms) 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 tantalum to be analyzed without the need for sample dissolution prior to analysis which greatly increases 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 tantalum oxide. 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 tantalum oxide. It is recommended that the sample preparation and analysis procedures outlined in this note also be followed for the analysis of tantalum metal, with the addition of an initial preparation step to convert tantalum metal to its oxide form. The conversion to tantalum oxide is recommended because the oxide form melts and boils more smoothly and reproducibly in an arc than does the metallic form.

Experimental

Instrumentation

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 samples were analyzed on the Teledyne Leeman Labs ***Prodigy DC Arc****.* The instrument was operated using the instrument and method parameters listed in Table 1. Standards were burned in air and all elements were integrated from 0-30 seconds.

All standards were prepared for analysis by mixing each with a carrier consisting of a 2:1 blend of high purity graphite powder and silver chloride. The standards were combined with the carrier such that the ratio of carrier to sample was 2:1. All mixtures were thoroughly blended in a mixer/mill for a minimum of 5 minutes before hand-packing them into sample electrodes. The packed electrodes were then dried in an oven at 100 ºC for 1 hour.

Table 1. DC Arc Operating Conditions

Parameter	Setting
DC Arc Stand	
Current	Ignite at 10A, hold at 10A for 30s
Stallwood Jet	None
Analytical Gap	3 mm
Electrodes	
Sample Electrode	3/16" in diameter with 4 mm x 3 mm undercut cup
Counter Electrode	1/8” diameter and pointed
Sample	
Internal Standard	None
Integration Time	0-30 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 a 4 mm x 3 mm undercut cup (part # S-15). The counter electrodes used for all analyses were 1/8” in diameter and pointed (part # C-1). A 3 mm analytical gap was used and the position of the electrodes was adjusted during the sample burn to maintain a distance of 3 mm between the sample and the counter electrode.

Calibration Standards

The instrument was calibrated with several high-purity tantalum oxide standards that were spiked with a multi-element stock standard containing 45 elements at 1.21% (MV Laboratories, Inc., Frenchtown, NJ). Calibration standards were prepared in this matrix by serial dilution on a weight-to-weight basis such that the analytes of interest were present at 0, 0.6, 6.4, 32 and 64 ppm in the tantalum oxide matrix. All standards were weighed, mixed and prepared for analysis as described above.

The DC Arc Technique for Ta 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 wavelengths of light. The time-varying intensity of that light yields 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 640 ppm multi-element standard in a tantalum oxide matrix obtained over the course of a DC Arc burn that lasted 60 seconds. The 640 ppm multi-element standard was used for obtaining TRA scans and was not used for calibration purposes.

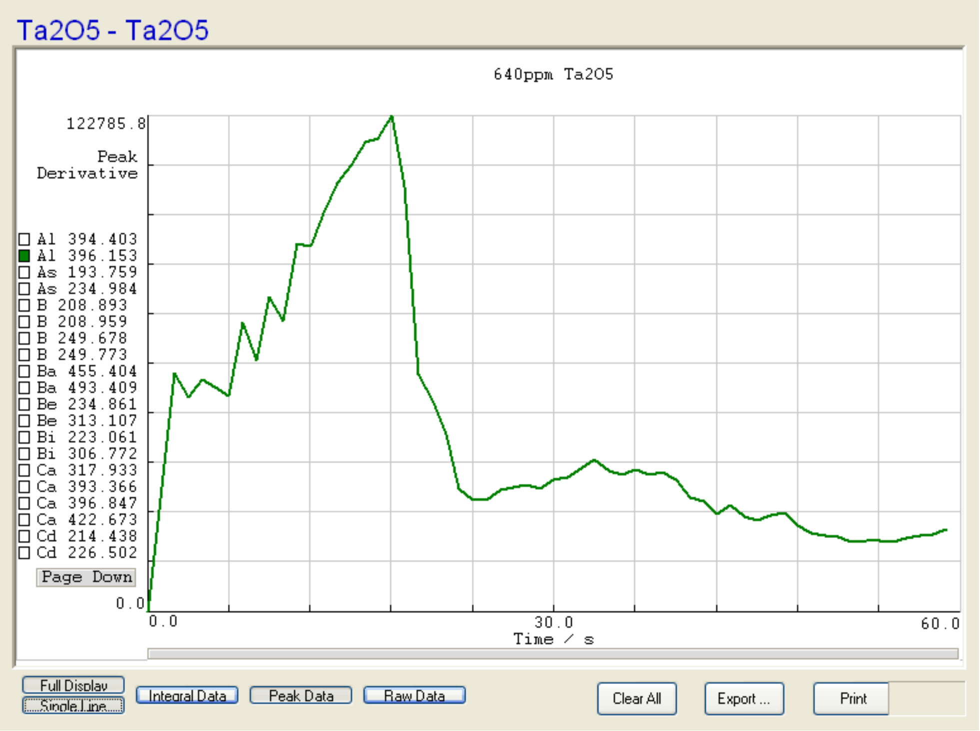


Figure 1. *Time-Resolved Analysis Scan of Al in a 640 ppm Calibration Standard*

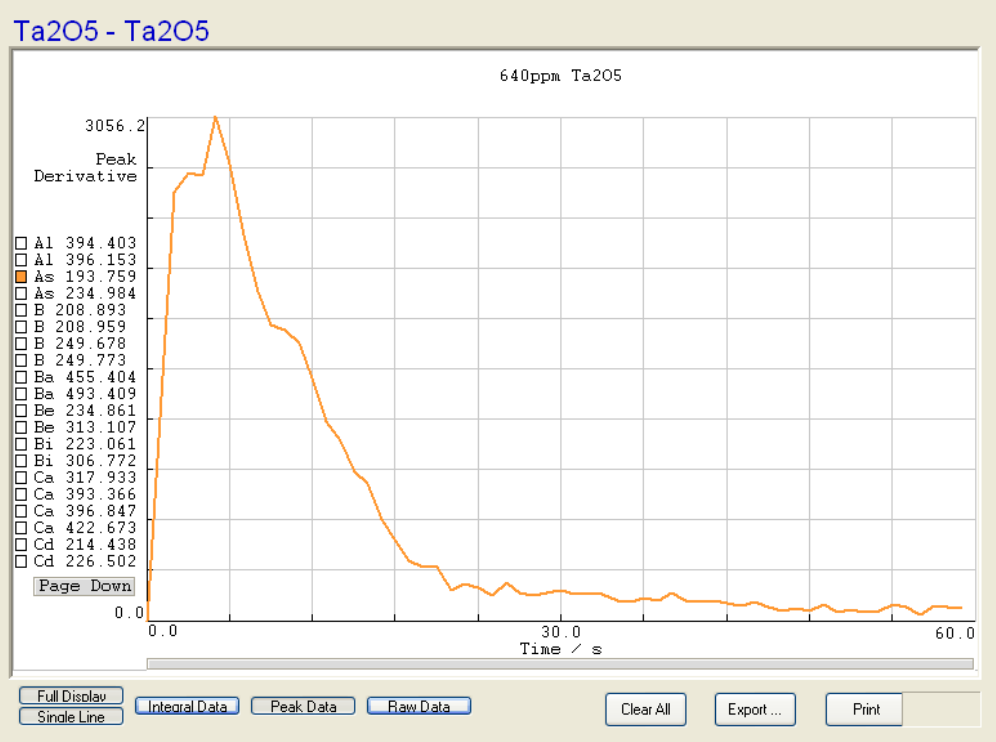


Figure 2. *Time-Resolved Analysis Scan of As in a 640 ppm Calibration Standard*

In Figures 1 and 2, data for the emission of Al at 396.153 nm and As at 193.759 nm, respectively, are plotted as a function of time. As illustrated above, the majority of the emission from both elements was observed during the first 30 seconds of the arc burn. All wavelengths were examined in this fashion and similar emission patterns were observed. For this reason, emission from all elements of interest was collected from 0-30 seconds. Those integration times are reiterated in Table 2 below.

Wavelength Parameters

The wavelengths and background correction points used in this method are outlined 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.

Element	Wavelength (nm)	Left Background Position	Right Background Position	Integration Time (s)
Al	396.153	---	13	0-30
As	193.759	---	13	0-30
B	249.678	5	---	0-30
Ba	455.404	---	14	0-30
Be	234.861	3	---	0-30
Bi	306.772	---	15	0-30
Ca	396.847	---	14	0-30
Cd	226.502	---	11	0-30
Co	345.351	---	15	0-30
Cu	324.754	---	15	0-30
Fe	271.903	---	11	0-30
Ge	303.906	1	---	0-30
K	766.491	---	12	0-30
Li	670.784	---	13	0-30
Mg	279.553	---	10	0-30
Mn	257.610	---	15	0-30
Na	588.995	3	---	0-30
Ni	300.249	2	---	0-30
Pb	283.307	---	12	0-30
Sb	217.589	4	---	0-30
Se	203.985	3	---	0-30
Sn	317.502	6	---	0-30
Sr	460.733	3	---	0-30
Te	214.275	---	15	0-30
Ti	337.280	3	---	0-30
V	318.398	5	---	0-30
Zn	213.856	3	---	0-30
Zr	339.198	---	15	0-30

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 Zn at 213.856 nm in the 6.4 ppm calibration standard. In Figure 3, the left background correction point is illustrated in blue at pixel position 3. 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.

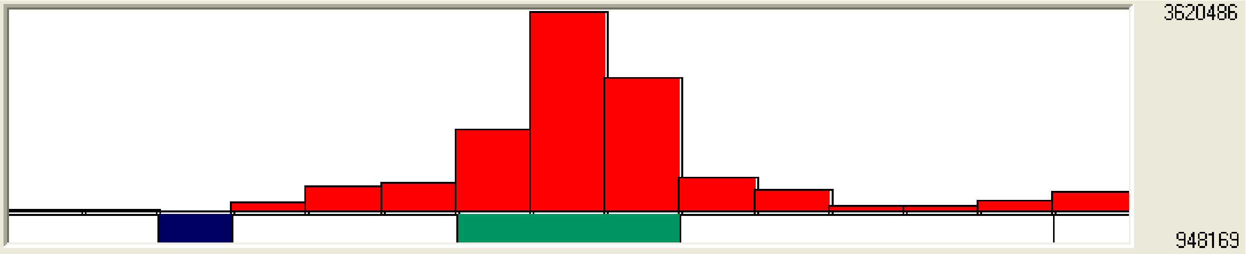
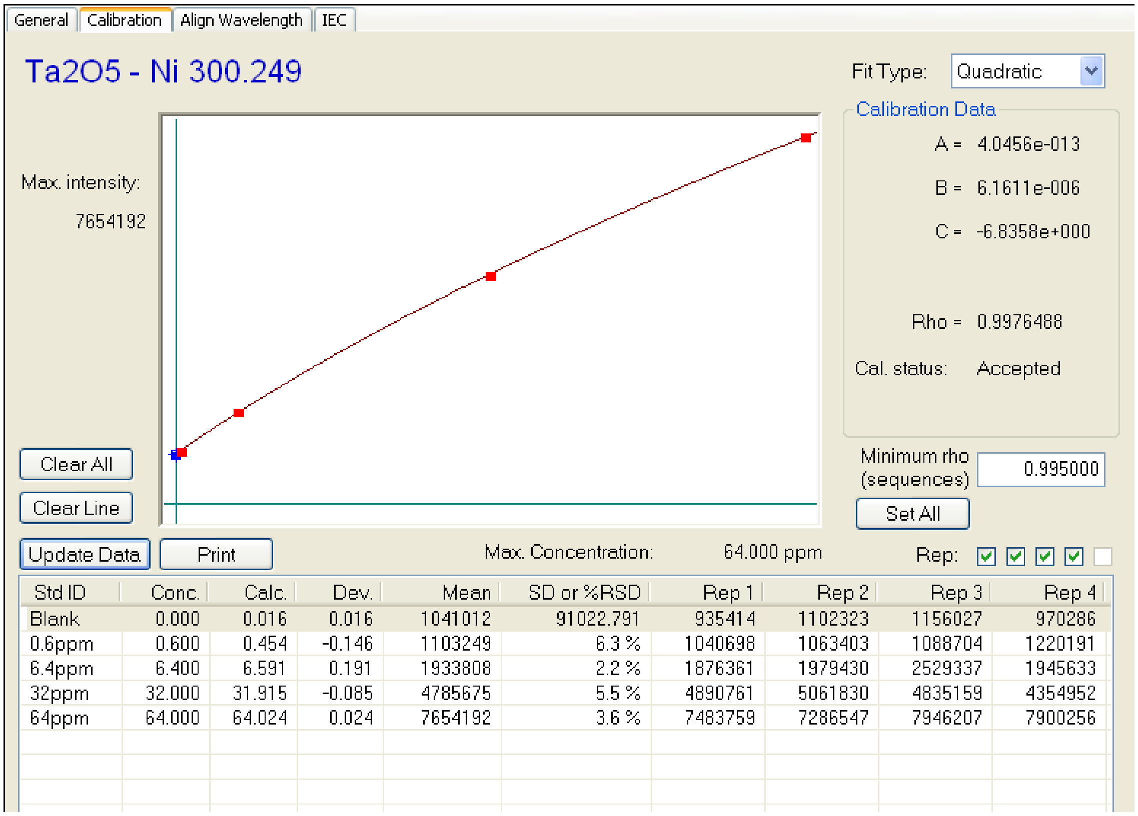


Figure 3. *Graphical Representation of the Zn 213.856 nm Subarray for the 6.4 ppm Calibration Standard*

Examples of typical calibration curves for elements measured in high purity tantalum oxide are illustrated in Figures 4 and 5. Figures 4 and 5 contain calibration curves for Ni at 300.249 nm and Pb at 283.307 nm, respectively, to demonstrate typical precision and accuracy for the analytes measured in this work.



Ta2O5 - Ni 300.249

Fit Type: Quadratic

Calibration Data

A = 4.0456e-013

B = 6.1611e-006

C = -6.8358e+000

Rho = 0.9976488

Cal. status: Accepted

Max. intensity: 7654192

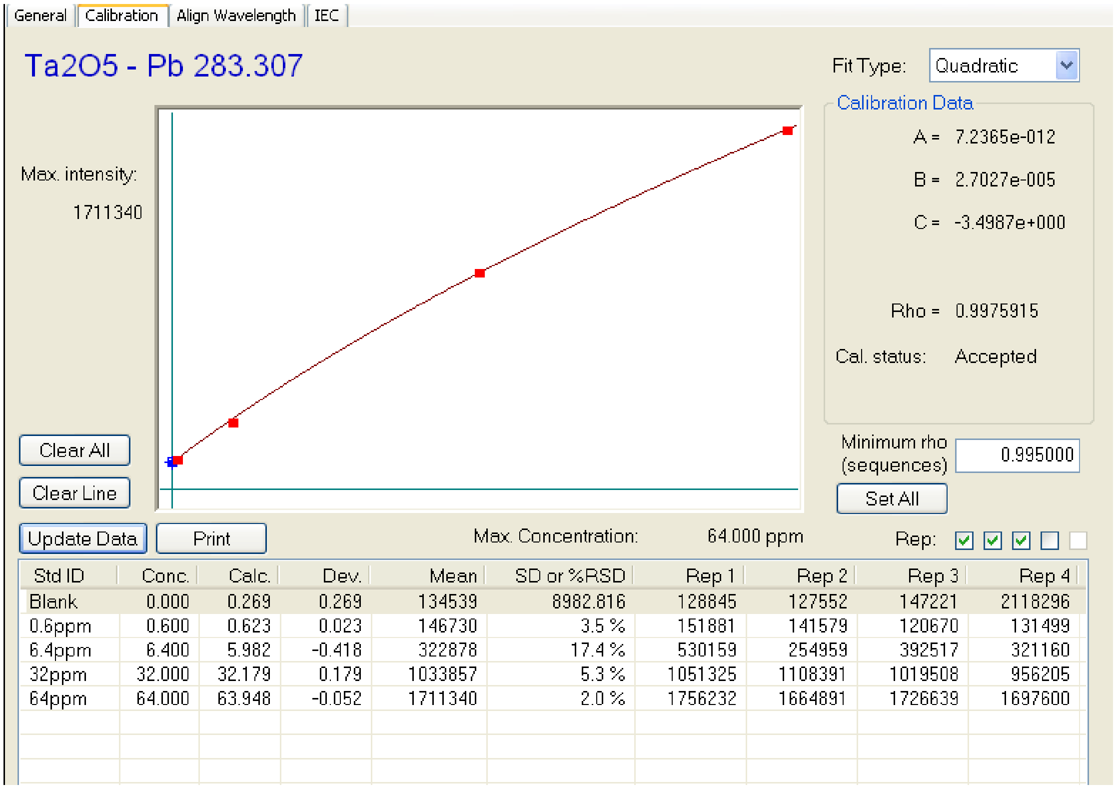
Minimum rho (sequences) 0.995000

Max. Concentration: 64.000 ppm

Rep: ☑ ☑ ☑ ☑ ☐

Std ID	Conc.	Calc.	Dev.	Mean	SD or %RSD	Rep 1	Rep 2	Rep 3	Rep 4
Blank	0.000	0.016	0.016	1041012	91022.791	935414	1102323	1156027	970286
0.6ppm	0.600	0.454	-0.146	1103249	6.3 %	1040698	1063403	1088704	1220191
6.4ppm	6.400	6.591	0.191	1933808	2.2 %	1876361	1979430	2529337	1945633
32ppm	32.000	31.915	-0.085	4785675	5.5 %	4890761	5061830	4835159	4354952
64ppm	64.000	64.024	0.024	7654192	3.6 %	7483759	7286547	7946207	7900256

Figure 4. *Calibration Curve of Ni at 300.249 nm in High Purity Tantalum Oxide*



Ta2O5 - Pb 283.307

Fit Type: Quadratic

Max. intensity: 1711340

Calibration Data

A = 7.2365e-012

B = 2.7027e-005

C = -3.4987e+000

Rho = 0.9975915

Cal. status: Accepted

Minimum rho (sequences) 0.995000

Max. Concentration: 64.000 ppm

Rep: ☑ ☑ ☑ ☐ ☐

Std ID	Conc.	Calc.	Dev.	Mean	SD or %RSD	Rep 1	Rep 2	Rep 3	Rep 4
Blank	0.000	0.269	0.269	134539	8982.816	128845	127552	147221	2118296
0.6ppm	0.600	0.623	0.023	146730	3.5 %	151881	141579	120670	131499
6.4ppm	6.400	5.982	-0.418	322878	17.4 %	530159	254959	392517	321160
32ppm	32.000	32.179	0.179	1033857	5.3 %	1051325	1108391	1019508	956205
64ppm	64.000	63.948	-0.052	1711340	2.0 %	1756232	1664891	1726639	1697600

Figure 5. *Calibration Curve of Pb at 283.307 nm in High Purity Tantalum 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). The detection limits for Na, Ni and Ti are slightly worse than expected and are presumed to be due to slight contamination in the tantalum oxide matrix used to produce the calibration standards in this study.

Element	Wavelength (nm)	Detection Limits (ppm)
Al	396.153	0.17
As	193.759	1.9
B	249.678	0.25
Ba	455.404	0.31
Be	234.861	0.13
Bi	306.772	0.23
Ca	396.847	0.21
Cd	226.502	0.86
Co	345.351	0.89
Cu	324.754	0.62
Fe	271.903	1.2
Ge	303.906	0.61
K	766.491	5.5
Li	670.784	0.09
Mg	279.553	0.40
Mn	257.610	0.74
Na	588.995	2.3
Ni	300.249	1.8
Pb	283.307	1.2
Sb	217.589	0.40
Se	203.985	3.8
Sn	317.502	0.54
Sr	460.733	0.62
Te	214.275	0.95
Ti	337.280	3.7
V	318.398	0.34
Zn	213.856	0.08
Zr	339.198	2.8

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

Conclusions

The analysis of tantalum oxide 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 tantalum oxide matrix.