



# Analysis of Trace Elements in High Purity Copper using the Teledyne Leeman Labs Prodigy DC Arc

## Introduction

Few other techniques can challenge the ease-of-use of DC Arc spectroscopy for the direct analysis of a wide range of solid materials. The earliest instruments, many of which are still in use today, relied on photographic plate detectors. These instruments provided a permanent photographic record of a sample's spectrum, but the plates were cumbersome and time-consuming to develop and interpret. These detectors were replaced by photomultiplier tubes (PMTs) which significantly improved sample throughput; however, measurements could not be made with simultaneous background correction nor could a complete record of the spectrum be collected.

The advent of solid-state array technology rivals the speed of the PMT detector-based DC Arc systems with the added benefit of providing a permanent record of the full DC Arc spectrum. The spectrometer used in this application note, the Prodigy DC Arc, provides full wavelength coverage and offers advantages such as: simultaneous background correction, the use of multiple wavelengths per element, the ability to perform time-resolved analysis and reduced analysis time per sample.

The analysis of trace elements in high purity copper 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. More importantly, they dilute the sample; often to such an extent that the analytes of interest are present in solution at levels below the detection limit of the technique being used to measure them. DC Arc allows copper 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 eliminates any sample dilution, resulting in better detection limits than those obtained with other analytical techniques.



This application note will demonstrate the ability of the Teledyne Leeman Labs Prodigy DC Arc spectrometer to determine trace elements in high purity copper. 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 high purity copper.

## 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 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 (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.

### Operator Parameters

The sample and counter electrodes were purchased from Bay Carbon Inc (Bay City, MI) and used as received. The sample electrodes were 1/4" in diameter with a crater and a 1" post (part # PD-1). The counter electrodes were 1/8" in diameter and pointed (part # C-1 ST-21). 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. All analyses were performed in air and without the use of a Stallwood jet.

The DC arc stand was operated with the current-controlled program listed in Table 1. All analyses were performed in forward polarity mode.

Step	Time (s)	Current (amp)
1	0	3
2	2	3
3	4	11
4	90	11

*Table 1. DC Arc Stand Power Conditions for Forward Polarity Mode*

## Experimental

### Calibration Standards

High-purity Cu standards were purchased from CopperSpec (Sandy, Utah) and used as received. The concentrations used for calibration are listed in Table 2. Copper was used as an internal standard for all sample analyses and the concentration present in each calibration standard is included in Table 2 below.

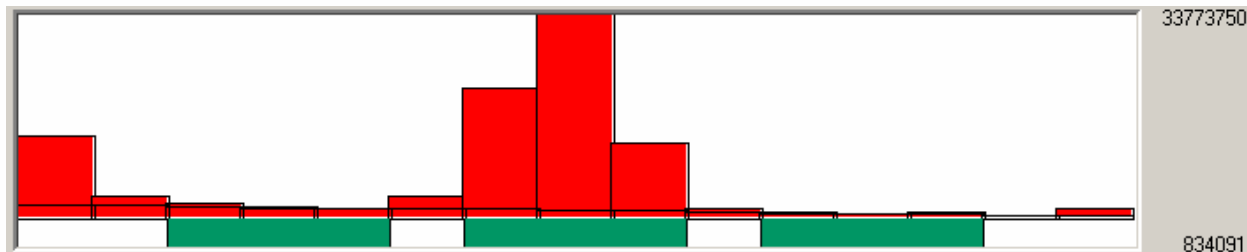
Element	Std 1 (ppm)	Std 2 (ppm)	Std 3 (ppm)	Std 4 (ppm)	Std 5 (ppm)	Std 6 (ppm)	Std 7 (ppm)	Std 8 (ppm)
Ag, As, Bi, Ni, Sb, Se, Sn, Te, Cu	0.1	0.5	1.0	3.0	5.0	10.0	20.0	50.0
Fe	0.1	0.5	1.8	3.0	6.0	10.0	20.0	50.0
Pb	0.1	0.6	1.0	3.7	5.0	10.0	20.0	50.0
Zn	0.1	0.5	1.0	3.0	4.8	10.0	18.7	37.0

*Table 2. Calibration Standards*

### Wavelength Parameters

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. In this work, the subarrays used for all data collection were 3 pixels tall and 15 pixels wide.

An example of the data collection that takes place in each subarray is illustrated graphically in Figure 1. This figure represents the data collected for Ag at 328.068 nm in the 1.0 ppm calibration standard. In Figure 1, the left and right background correction points are illustrated at pixel positions 3 and 11, each with a width of 3. The pixels used for integrating the analytical peak are at positions 7, 8 and 9.



**Figure 1.** Graphical Representation of the Ag 328.068 nm Subarray for the 1.0 ppm Calibration Standard

The wavelengths and background correction points used in this method are outlined in Table 3. Information regarding the integration time used for the analysis of each element is also listed in Table 3. For elements in which background correction included more than 1 pixel on the same side, multiple values are listed to indicate the positions for all the pixels used. 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 Cu

DC Arc is a distillation technique that allows the 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 distillation profile that can be measured by the optical spectrometer. This phenomenon is shown in Figures 2 and 3, below. These distillation profiles can be used for choosing integration time periods that maximize the signal to noise ratio for each analyte of interest. For this work, elements were grouped into one of two integration periods based on the results obtained from time-resolved analysis (TRA) scans of a 50.0 ppm calibration standard. Scans were obtained over the course of a DC Arc burn lasting 120 seconds and two examples of these scans are illustrated in Figures 2 and 3. Elements that were observed to boil off relatively quickly (see Figure 2) were collected into the first timing group and emission from those elements was collected for the first 10 seconds of the DC Arc burn. Elements that were collected into the second timing group were more refractory in nature and emitted light for a relatively long period of time as they slowly boiled off (see Figure 3). Data for these elements was collected for the last 80 seconds of the DC Arc burn. The Cu matrix boiled throughout the DC Arc burn and allowed for the use of a Cu internal standard for both timing groups.

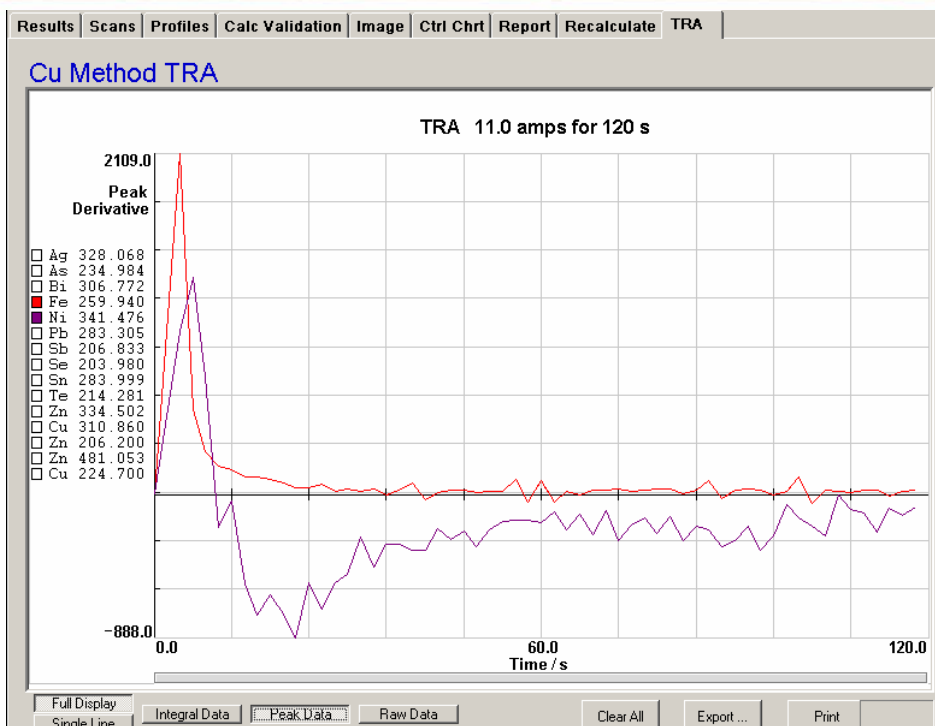


Figure 2. Time-Resolved Analysis Scan of Fe and Ni in the 50.0 ppm Calibration Standard

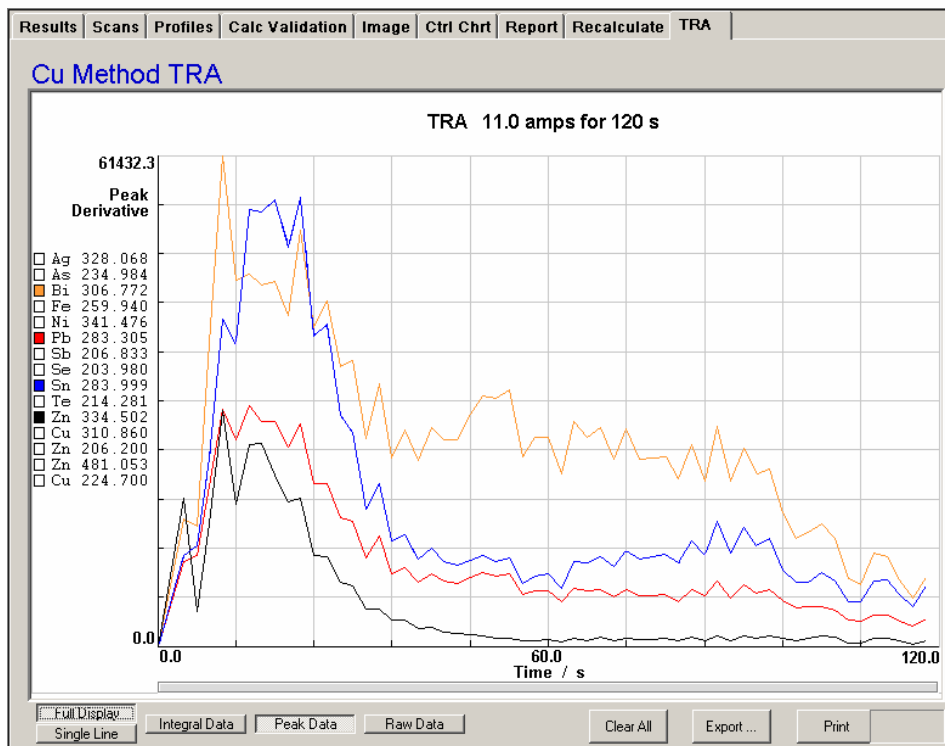


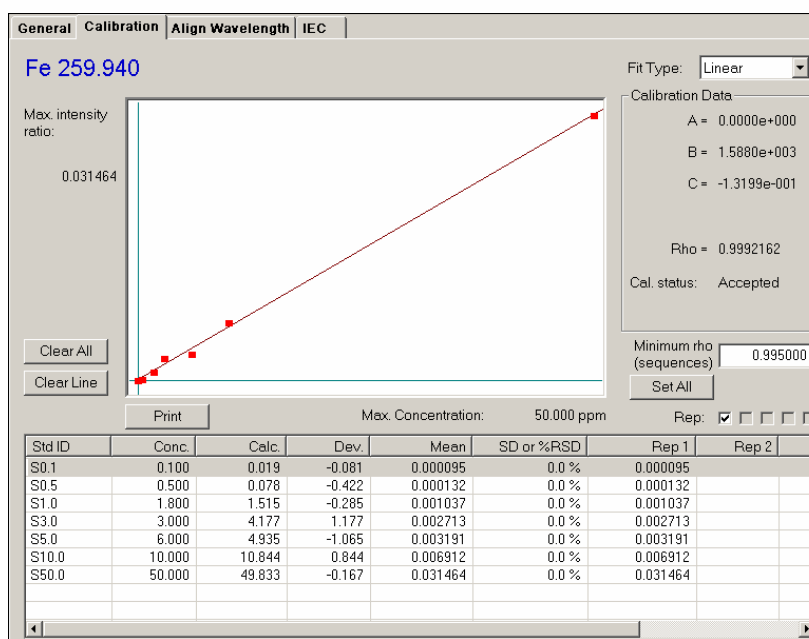
Figure 3. Time-Resolved Analysis Scan of Bi, Pb, Sn and Zn in the 50.0 ppm Calibration Standard

As indicated in Table 3, all analytes of interest were grouped into 1 of 2 integration periods. Elements included in the second timing group (integration commenced 10 s after igniting the DC arc and continuing for 80 s) are denoted with a "2" following the wavelength listing in Table 3.

Element	Wavelength (nm)	Left Background Position	Right Background Position	Integration Period (s)
Ag	328.068 (2)	3-5	13	10-90
As	234.984 (2)	1-3	12-14	10-90
Bi	306.772 (2)	4-6	11-13	10-90
Fe	259.940	5-6	11-13	0-10
Ni	305.082	3-5	11-13	0-10
Pb	283.305 (2)	5-6	11-13	10-90
Sb	231.147 (2)	4-6	11-13	10-90
Se	203.980 (2)	3-5	10-12	10-90
Sn	283.999 (2)	3-5	11-14	10-90
Te	214.281 (2)	6	10-12	10-90
Zn	481.053 (2)	4-6	11-13	10-90
Cu	310.860	1-3	13-15	0-10
Cu	310.860 (2)	3-4	13-15	10-90

**Table 3.** Wavelengths, Background Correction Points and Integration Times Used

Examples of typical calibration curves for elements measured in high purity copper are illustrated in Figures 4-6. Figure 4 contains a calibration curve for Fe at 259.940 nm to demonstrate typical precision and linearity for elements measured in the first timing group. Figures 5 and 6 contain calibration curves for Bi at 306.772 nm and Se at 203.980 nm, respectively, to demonstrate typical precision and linearity for elements measured in the second timing group.



**Figure 4.** Calibration Curve of Fe at 259.940 nm in High Purity Cu

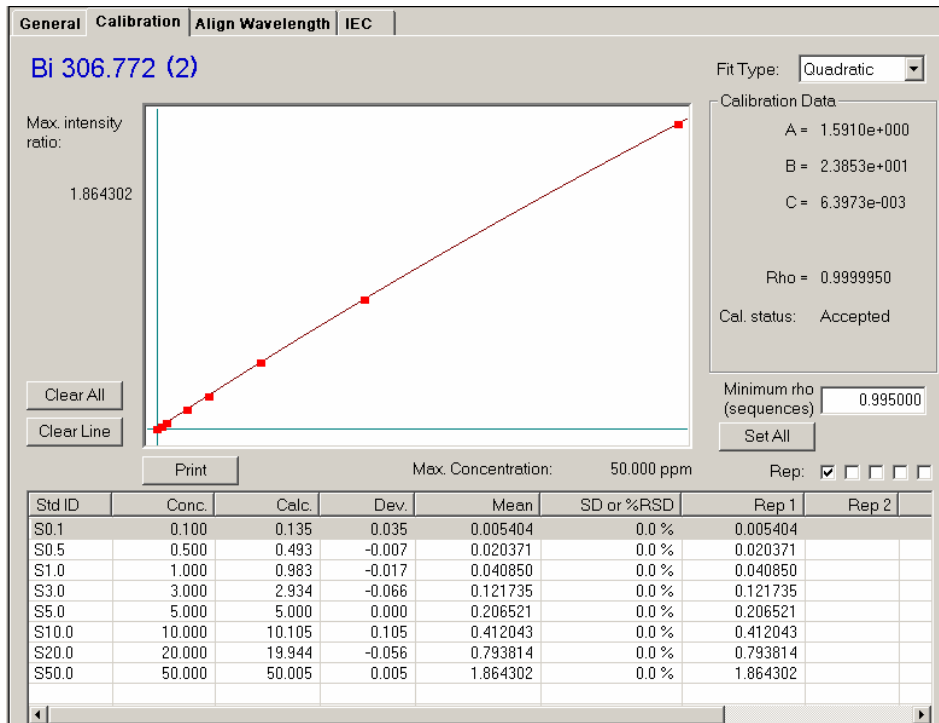


Figure 5. Calibration Curve of Bi at 306.772 nm in High Purity Cu

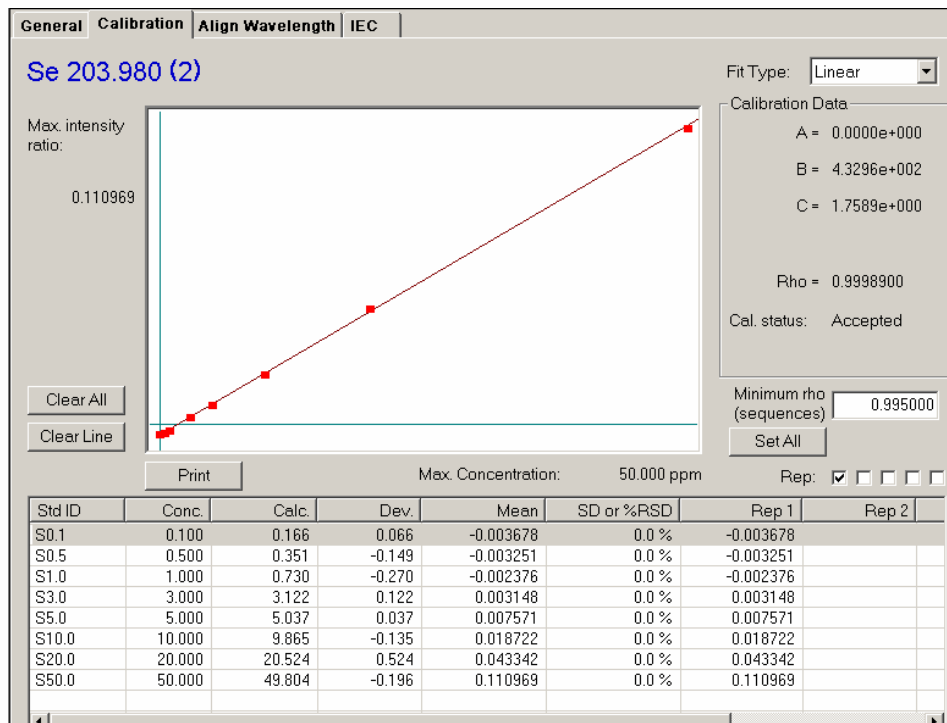


Figure 6. Calibration Curve of Se at 203.980 nm in High Purity Cu

## Results and Discussions

### 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 lowest calibration standard (0.1 ppm). Results for the detection limit study are listed in Table 4 and are listed in units of parts per million (ppm).

Element	Wavelength (nm)	Detection Limit (ppm)
Ag	328.068 (2)	0.02
As	234.984 (2)	1.1
Bi	306.772 (2)	0.015
Fe	259.940	0.2
Ni	305.082	0.2
Pb	283.305 (2)	0.02
Sb	231.147 (2)	0.25
Se	203.980 (2)	0.4
Sn	283.999 (2)	0.03
Te	214.281 (2)	0.1
Zn	481.053 (2)	0.07

*Table 4. Detection Limits in High Purity Cu*

### Conclusions

The analysis of high purity Cu has been successfully performed using the Teledyne Leeman Labs Prodigy DC Arc Spectrometer. The use of 2 integration periods allowed for emission from volatile elements to be collected separately from emission from more refractory elements which improved the overall sensitivity and detection limits for the method. The results presented in this work indicate that the instrument's detection limits for all measured analytes were well below 1 ppm.

As reflected in the detection limit data, the current-controlled DC Arc power supply, combined with the simultaneous data collection of both peak and background data, provides exceptionally reproducible sample burns and precise results.