



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, these procedures 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 mm², 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 platform electrodes with a 5/16" post (part # PD-1, see photo in Introduction section). 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.

The instrument was operated using the conditions outlined in Table 1. All analyses were performed in air and without the use of a Stallwood Jet. Nitrogen was used to purge the optical path between the DC Arc and the spectrometer's optical entrance window. This gas was used for the first 20 s of the DC Arc burn, at a flow rate of 1.5 L/min in order to analyze for sulfur at 180.7 nm. After 20 s, the nitrogen flow rate was reduced to 0 L/min and the remaining 80 s of the burn was performed without a gas for the purged optical path.

| Parameter | Setting |
|---------------------|--|
| DC Arc Stand | |
| Current | Ignition at 6 amps, constant 10.5 amps for 100 s |
| Purge Gas | 1.5 L/min N ₂ for 20 s, 0 L/min N ₂ for 80 s |
| Analytical Gap | 4 mm |
| Electrodes | |
| Sample Electrode | Platform with a 5/16" post |
| Counter Electrode | 1/8" in diameter and pointed |
| Sample | |
| Sample Size | 250 mg +/- 20 mg |
| Integration Time | 100 s for all elements |

Table 1. DC Arc Operating Conditions

Calibration Standards

The instrument was calibrated with a multitude of high-purity Cu standards that contained the analytes of interest at concentrations that ranged from 0.01 – 100.0 ppm. The Cu standards consisted of certified reference materials produced from unalloyed Cu rods and were used as received. Standards were obtained from NIST, formerly known as NBS (NIST 494, 495 and 496), and CopperSpec (CS001, CS005, CS010, CS030, CS050, CS100, CS200 and CS500).

The instrument was calibrated for S using ALCATEL and NBS standards as the CopperSpec standards did not contain certified values for S. Once the instrument was calibrated for S, the CopperSpec standards were analyzed as unknown samples and the calculated S concentrations were built into the calibration curve. The resulting calibration curve for S is illustrated in Figure 3 below.

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 Cu

For the analysis of high purity Cu samples, the DC Arc allows the emission from 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 volatilized 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. These distillation profiles can be used for choosing integration time periods that maximize the signal to noise ratio for each analyte of interest. An example distillation profile is shown in Figure 1. The figure is based on a time-resolved analysis (TRA) scan of a 50.0 ppm

Cu standard obtained over the course of a DC Arc burn that lasted 100 seconds. For simplicity, only 4 wavelengths were chosen for illustration.

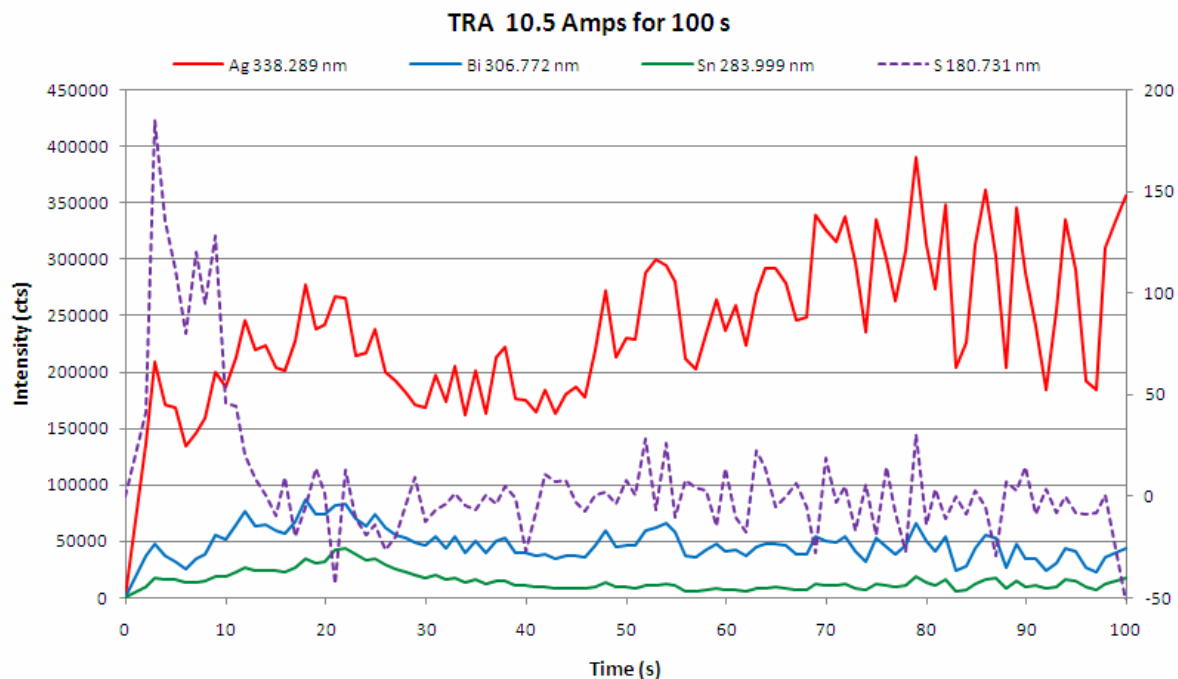


Figure 1. Time-Resolved Analysis Scan of Ag, Bi, S and Sn in the 50.0 ppm Calibration Standard

In Figure 1, data for Ag, Bi and Sn is plotted on the primary axis using solid lines. Data for S is plotted on the secondary axis using dashed lines. Based on the data in Figure 1, all analytes of interest were grouped into a single, 100-second integration period and nitrogen was used to purge the optical path for the first 20 seconds of the arc burn.

The use of a moderate flow (1.5 L/min) of nitrogen effectively removed air from the optical path which allowed emission from S to be collected. However, the use of a purge gas reduced the stability of the DC Arc and caused it to wander around the sample more than it would have without the use of a purge gas. For this reason, the nitrogen flow was reduced to 0 L/min after the majority of S emission was complete and data collection for the remainder of the burn was conducted without a purged optical path.

| Element | Wavelength (nm) | Left Background Position | Right Background Position | Integration Period (s) |
|---------|-----------------|--------------------------|---------------------------|------------------------|
| Ag | 338.289 | 3 | 13 | 0-100 |
| As | 193.759 | --- | 14 | 0-100 |
| Bi | 306.772 | 2 | --- | 0-100 |
| Fe | 248.327 | 2 | --- | 0-100 |
| Ni | 305.082 | --- | 11 | 0-100 |
| Pb | 283.305 | --- | 15 | 0-100 |
| S | 180.731 | 1 | --- | 0-100 |
| Sb | 206.833 | 3 | --- | 0-100 |
| Se | 203.980 | --- | 17 | 0-100 |

| Element | Wavelength (nm) | Left Background Position | Right Background Position | Integration Period (s) |
|---------|-----------------|--------------------------|---------------------------|------------------------|
| Sn | 283.999 | --- | 14 | 0-100 |
| Te | 238.578 | --- | 13 | 0-100 |
| Zn | 481.053 | 3 | 13 | 0-100 |

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. 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 2. This figure represents the data collected for Ag at 338.289 nm in the 0.5 ppm calibration standard. In Figure 2, the left and right background correction points are illustrated in blue at pixel positions 3 and 13, each with a width of 1. The pixels used for integrating the analytical peak are illustrated in green at positions 7 and 8.

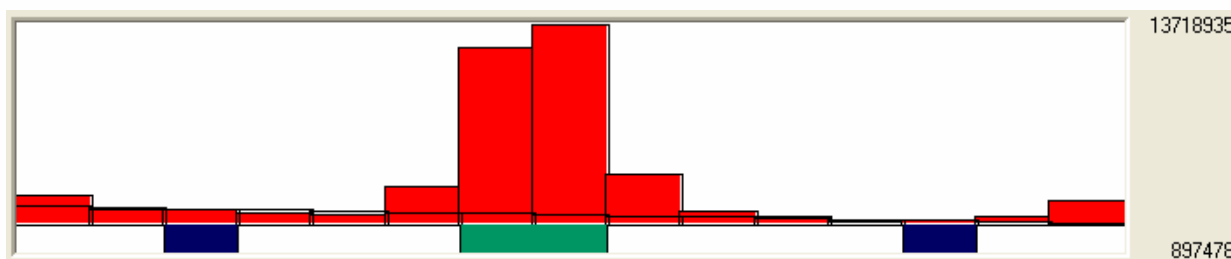


Figure 2. Graphical Representation of the Ag 338.289 nm Subarray for the 0.5 ppm Calibration Standard

Examples of typical calibration curves for elements measured in high purity copper are illustrated in Figures 3-6. Figures 3-6 contain calibration curves for S at 180.731 nm, Ag at 338.289 nm, As at 193.759 nm and Bi at 306.772 nm, respectively, to demonstrate typical precision and accuracy for the concentrations over which the instrument was calibrated.

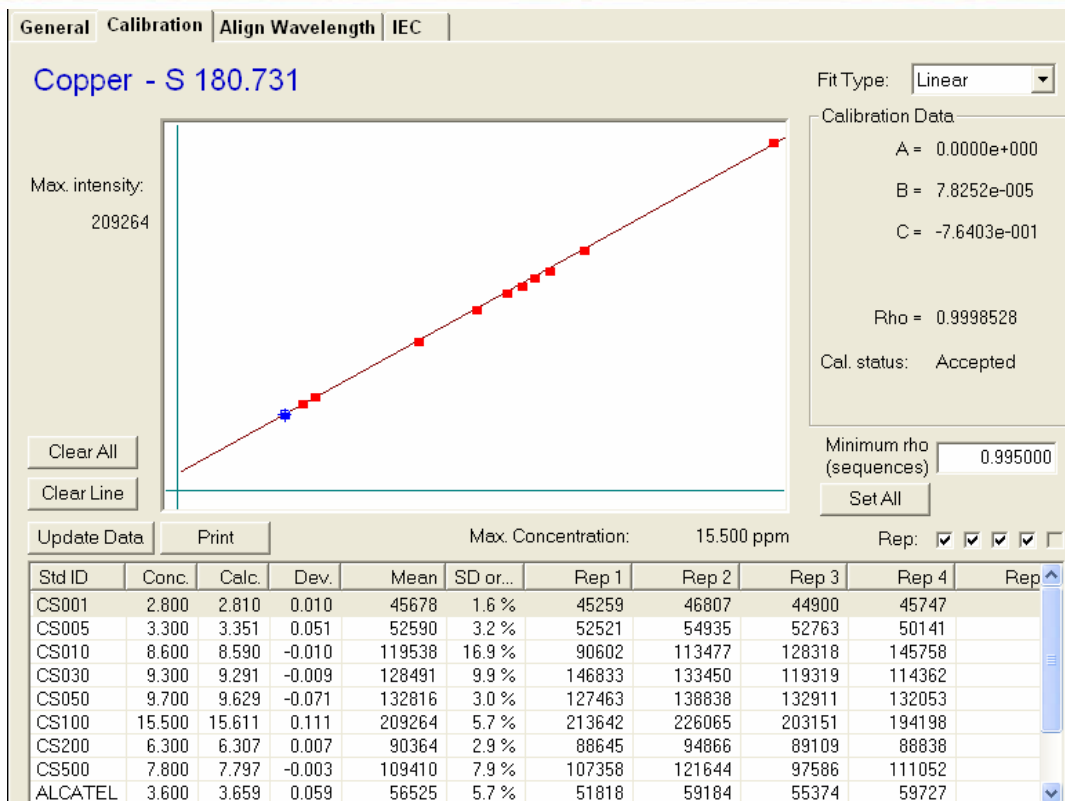


Figure 3. Calibration Curve of S at 180.731 nm in High Purity Cu

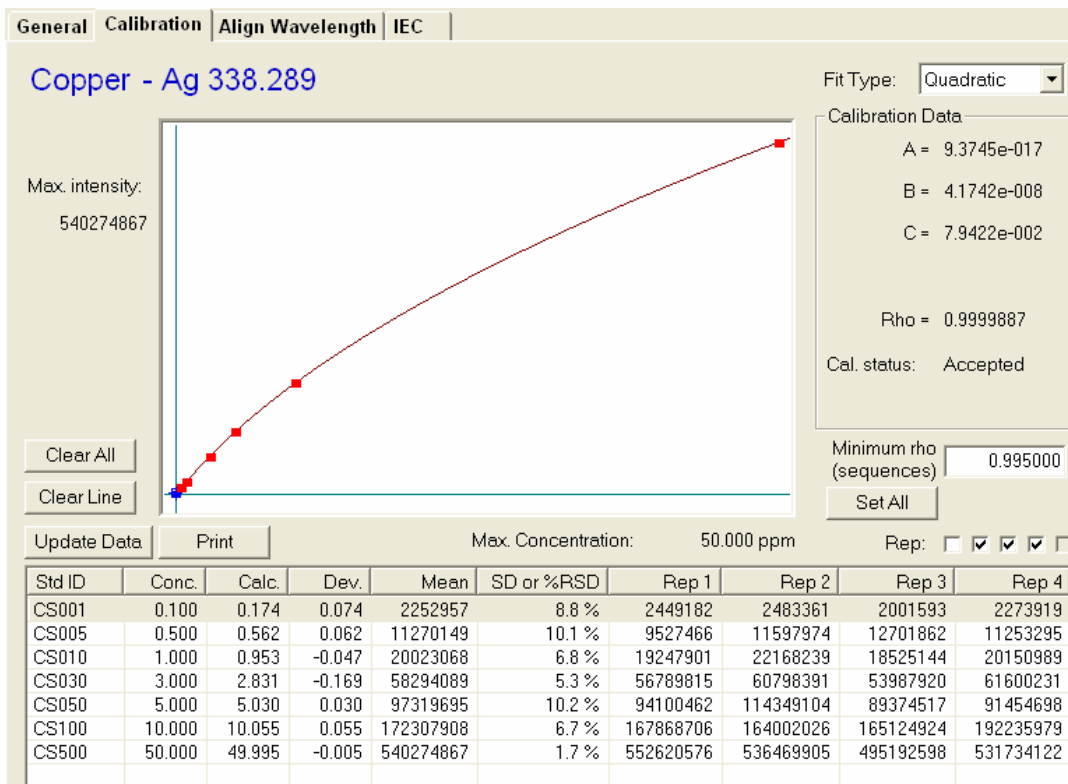


Figure 4. Calibration Curve of Ag at 338.289 nm in High Purity Cu

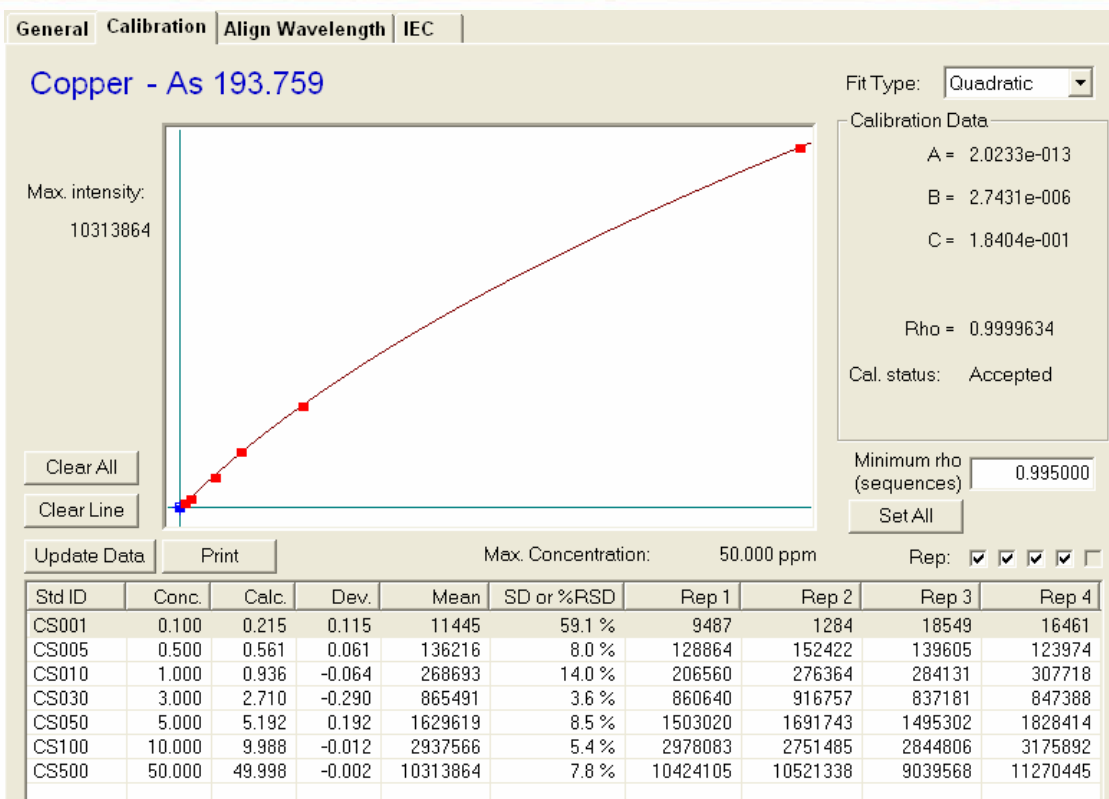


Figure 5. Calibration Curve of As at 193.759 nm in High Purity Cu

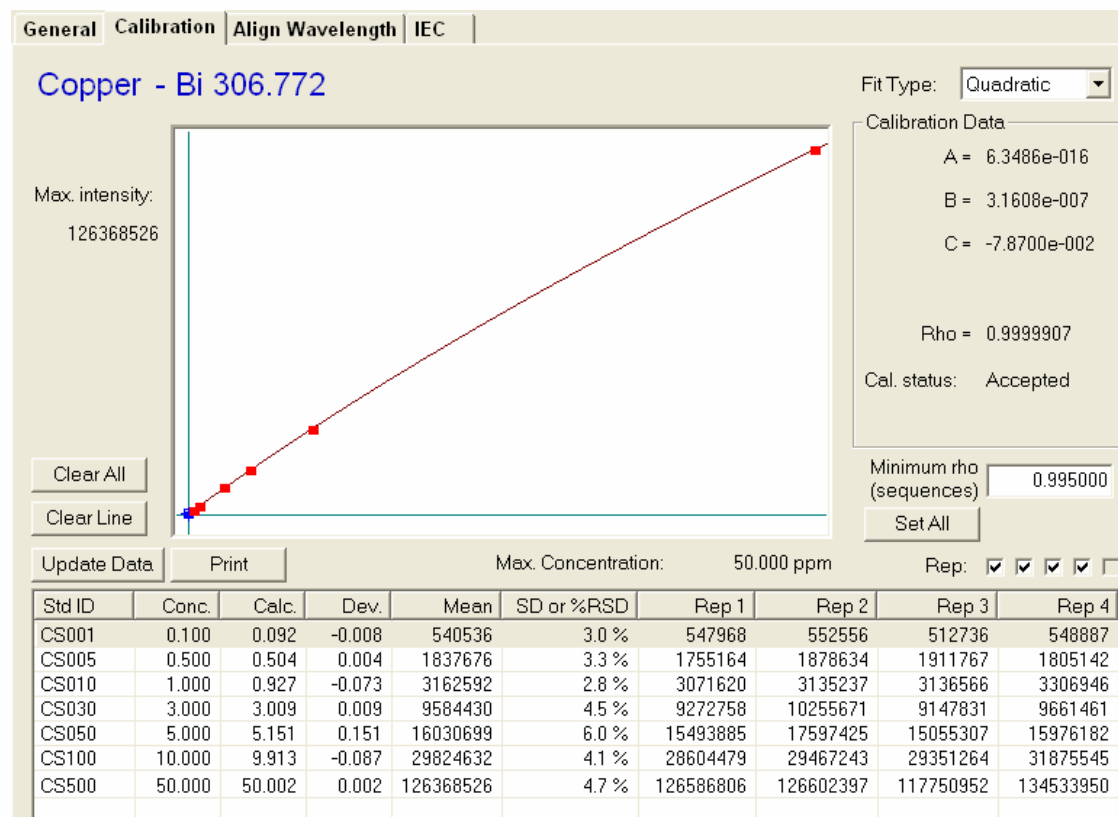


Figure 6. Calibration Curve of Bi at 306.772 nm in High Purity Cu

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 3 and are listed in units of parts per million (ppm).

| Element | Wavelength (nm) | Detection Limit (ppm) |
|---------|-----------------|-----------------------|
| Ag | 338.289 | 0.02 |
| As | 193.759 | 0.06 |
| Bi | 306.772 | 0.016 |
| Fe | 248.327 | 0.09 |
| Ni | 305.082 | 0.2 |
| Pb | 283.305 | 0.015 |
| S | 180.731 | 0.6 |
| Sb | 206.833 | 0.4 |
| Se | 203.980 | 0.8 |
| Sn | 283.999 | 0.05 |
| Te | 238.578 | 0.2 |
| Zn | 481.053 | 0.04 |

Table 3. 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 a nitrogen-purged optical path allowed for the determination of S with sub-ppm detection limits, which has never before been published. Furthermore, results indicate that the use of the nitrogen purge gas did not adversely affect the sensitivity and precision of the other analytes of interest. 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.