



Analysis of Trace Elements in High Purity Silver using the Prodigy DC Arc Spectrometer

Introduction

Silver is a white, relatively soft metal that has the highest electrical and thermal conductivity of all metals in the periodic table. Silver occurs naturally as the pure metal, as well as an alloyed metal with various metals in minerals such as chlorargyrite and argentite. The most common source of silver metal is as a byproduct of gold, lead, copper and zinc refinement.



The electrical and thermal conductivity properties of silver, along with its monetary value and lustrous appearance, make it suitable for use in many applications, both in its pure metallic form and as a compound in alloyed metals. As a pure metal, silver is used to produce currency, jewelry, sterling silver silverware, electrical contacts, and industrial catalysts. Layers of silver can be sputtered onto glass surfaces to produce optics that allow varying amounts of light penetration. Silver can also be used as a surface for mirrors to improve their reflectivity.

As an alloyed metal, silver can be combined with metals such as tin and mercury to produce amalgams used in dentistry applications. Silver alloys are also used in speaker wires, RF connectors, printed circuits, RFID antennas, high voltage contacts and electrical contacts inside computer keyboards. Silver is also used in nitrates and halides which are used in photography applications.

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

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 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 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

Standards were in the form of silver beads and were analyzed in their native form without the addition of graphite or a powdered internal standard. Standards were carefully weighed such that 100 mg of sample was transferred into each appropriate sample electrode. All analyses were performed on the Teledyne Leeman Labs **Prodigy DC Arc** in air without the use of a Stallwood Jet. 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
DC Arc Stand	
Current	Ignition at 13A, hold for 60 s, jump to 16A, hold for 65 s
Analytical Gap	4 mm
Electrodes	
Sample Electrode	3/16" in diameter with an undercut cup
Counter Electrode	1/8" diameter and pointed
Sample	
Sample Size	100 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 3/16" diameter electrodes with undercut cups (part # S-15). 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 two sets of high-purity silver standards. The first set of standards (Ag-1, Ag-2, Ag-3) contained the analytes of interest at concentrations that ranged from 0.01 to 213 ppm and was used to calibrate the instrument for purposes of calculating detection limits. The second set of standards (Blank, 1, 2, 3, 4, 5 and 6) contained the analytes of interest at concentrations that ranged from 1 to 1050 ppm and was used to determine the instrument's accuracy and working dynamic range in this matrix. All standards were analyzed as received and weighed directly into sample electrodes as described above.

The DC Arc Technique for Ag

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 of such a time profile is shown in Figure 1. The figure is based on a time-resolved analysis (TRA) scan of gold in the Ag-3 standard obtained over the course of a DC Arc burn that lasted 125 seconds.

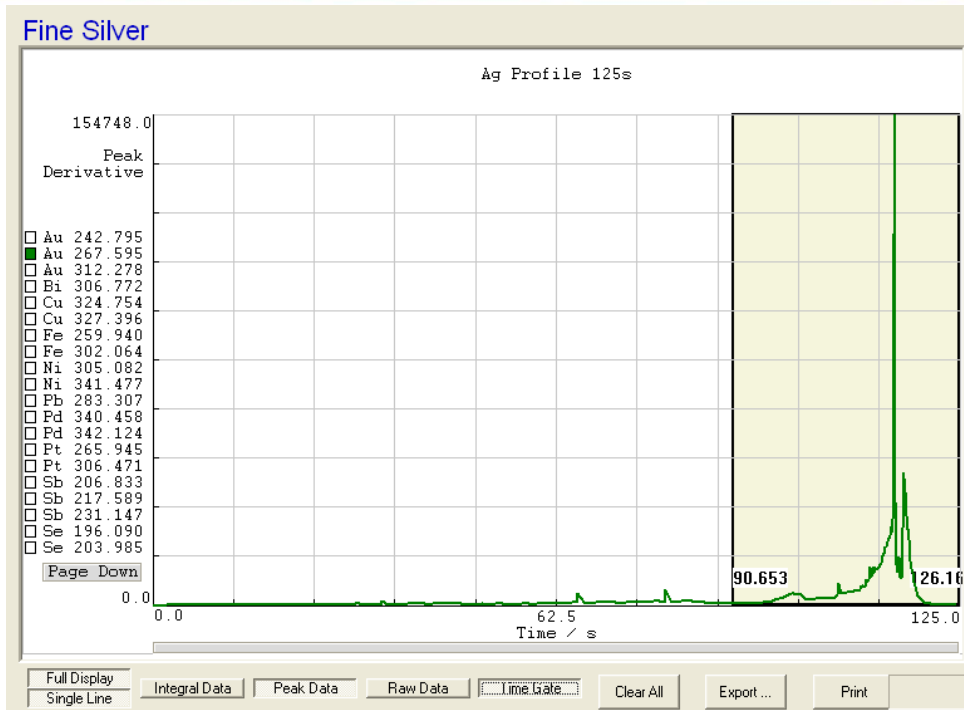


Figure 1. Time-Resolved Analysis Scan of the Ag-3 Calibration Standard

In Figure 1, data for the emission of Au at 267.595 nm is plotted as a function of time. As illustrated above, the majority of the emission from Au was observed during the last 35 seconds of the arc burn. For this reason, emission from this element was collected from 90-125 seconds. All wavelengths were examined in this fashion and suitable integration periods were chosen for each. Those time gates are listed in Table 2 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.

Element	Wavelength (nm)	Left Background Position	Right Background Position	Integration Time (s)
Au	267.595	1	15	90-125
Bi	306.772	---	15	0-60
Cu	324.754	1	15	0-120
Fe	302.064	1	---	0-125
Ni	305.082	2	13	90-125
Pb	283.307	---	15	0-45
Pd	340.458	3	---	90-125
Pt	265.945	3	---	90-125
Sb	217.589	4	---	0-125
Se	203.985	---	13	0-45
Sn	283.999	3	14	0-45
Te	214.275	---	15	0-125
Tl	535.046	---	13	0-25
Zn	481.053	3	---	0-20

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 Au at 267.595 nm in the Ag-3 ppm calibration standard. In Figure 2, the left and right background correction points are illustrated in blue at pixel positions 1 and 15, respectively. The pixels used for integrating the analytical peak are illustrated in green at positions 8, 9 and 10.

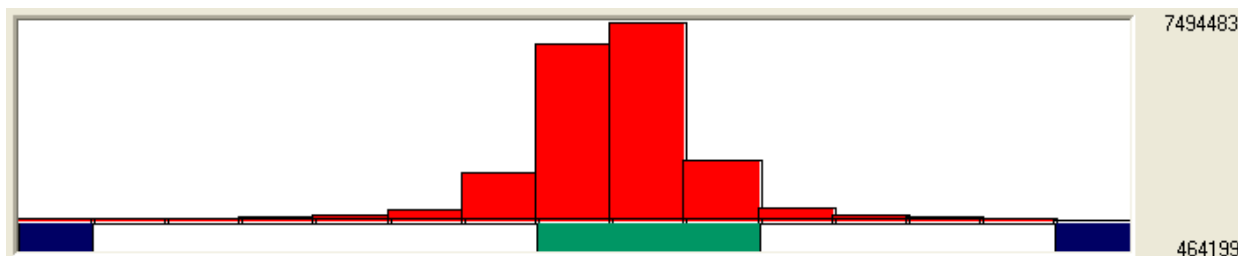


Figure 2. Graphical Representation of the Au 267.595 nm Subarray for the Ag-3 ppm Calibration Std

Examples of typical calibration curves for elements measured in high purity silver are illustrated in Figures 3 and 4 for Bi at 306.772 nm and Pb at 283.307 nm, respectively. The calibration curve for Bi indicates typical sensitivity observed when the first set of standards was used for calibration. The calibration curve for Pb demonstrates typical precision and accuracy when the instrument was calibrated using the second set of standards.

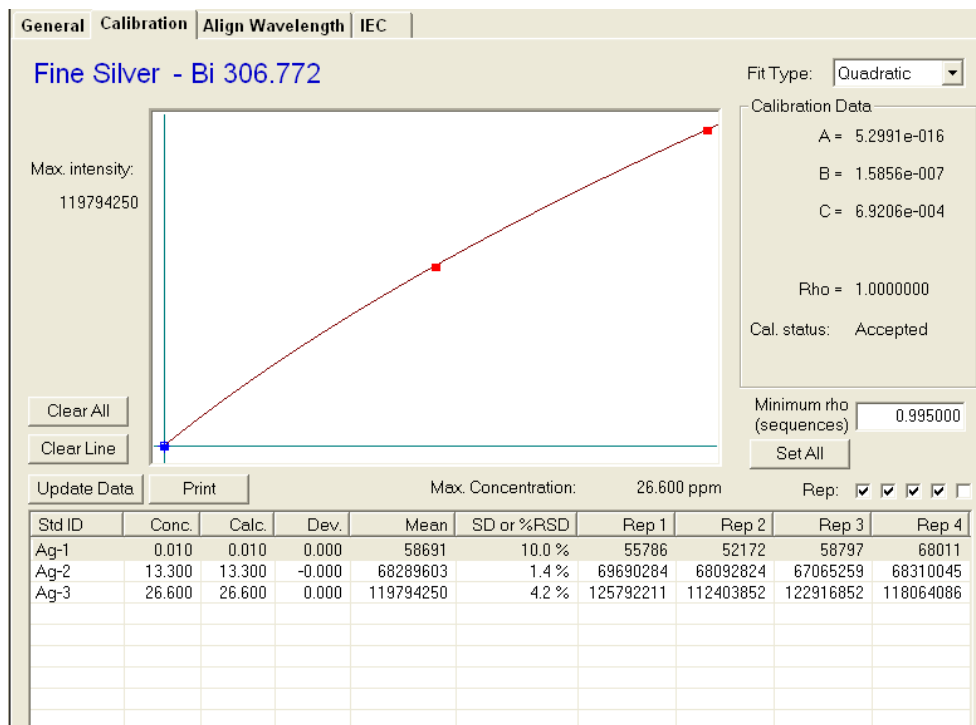


Figure 3. Calibration Curve of Bi at 306.772 nm in High Purity Silver

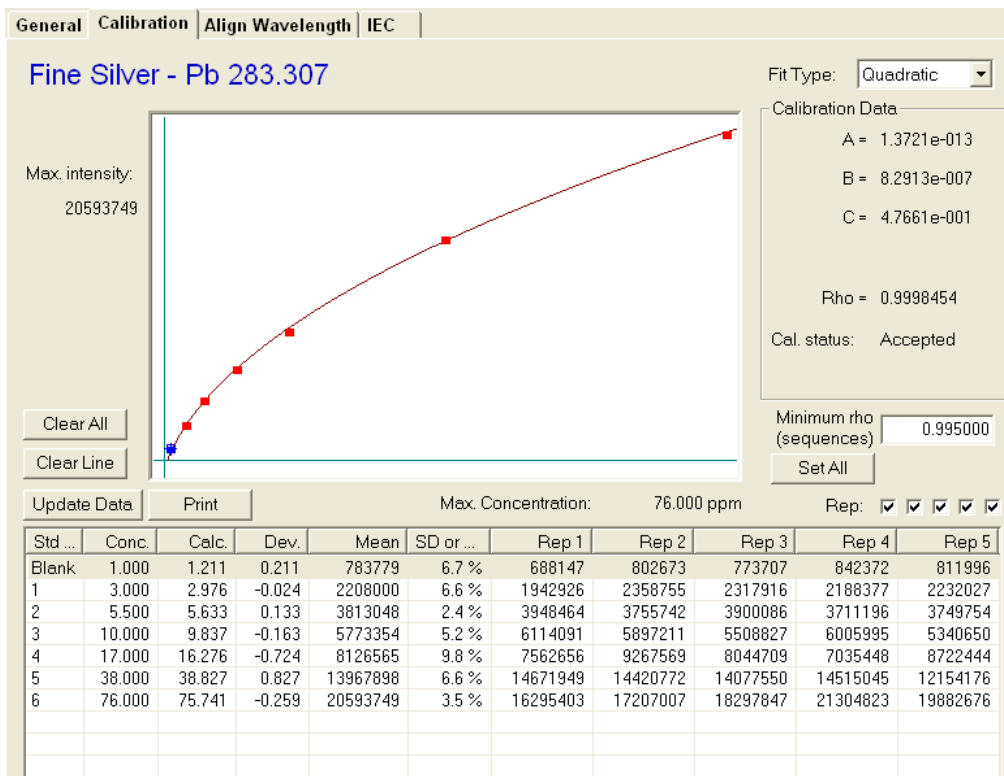


Figure 4. Calibration Curve of Pb at 283.307 nm in High Purity Silver

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 10 replicate measurements of the Ag-1 standard which contained all elements of interest at approximately 0.01 ppm. Results for the detection limit study are listed in Table 3 in units of parts per million (ppm).

Element	Wavelength (nm)	Detection Limits (ppm)
Au	267.595	0.01
Bi	306.772	0.003
Cu	324.754	0.01
Fe	302.064	0.2
Ni	305.082	0.006
Pb	283.307	0.007
Pd	340.458	0.002
Pt	265.945	0.02
Sb	217.589	0.2
Se	203.985	0.3
Sn	283.999	0.008
Te	214.275	0.2
Tl	535.046	0.3
Zn	481.053	0.02

Table 3. Detection Limits in High Purity Silver

Conclusions

The analysis of silver 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 silver metal matrix. The instrument's superior working dynamic range allows elements to be measured at concentrations that span multiple orders of magnitude without the need for line switching using multiple calibration curves.

It should be noted that the detection limits reported in this application note, reflect not only the precision and sensitivity of the instrument, but the homogeneity and the size uniformity of the standards used in the detection limit study. Standards that are less homogenous and uniform in size will cause the detection limits to deteriorate. The degree of deterioration will depend upon the variation in material size and composition.