



Analysis of Trace Elements in Cobalt Metal using the Teledyne Leeman Labs Prodigy DC Arc

Introduction

Cobalt is a hard, silver gray metal that melts at 1495 °C. Cobalt is a byproduct of mining iron, nickel, lead, silver and copper ores and does not naturally occur as the free metal. As a pure metal, cobalt is used in electroplating applications to create hard, oxidation resistant surfaces. Due to its magnetic, corrosion-resistant and wear-resistant properties, along with its strength at relatively high temperatures, cobalt is predominantly used as an alloyed metal.

The majority of cobalt-based alloys are temperature-stable, wear-resistant superalloys based upon combinations with nickel, chromium, tungsten or molybdenum. These alloys are used in the production of industrial catalysts, gas turbine blades, jet aircraft engines and prosthetic parts for joint replacement and dental applications. Samarium-cobalt and iron-cobalt alloys are used to produce permanent magnets.



Cobalt is also used in paints, pigments and inks which are used to tint glass and jewelry. Cobalt as cobalt(II) aluminate (CoAl_2O_4) produces a deep blue color, while a mixture of cobalt(II) oxide and zinc oxide produces a deep green color. The addition of cobalt enhances the stability of the pigment in addition to changing its color.

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

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 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** 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 standards and samples were analyzed in their native form without the addition of graphite or a powdered internal standard on a Teledyne Leeman Labs **Prodigy DC Arc**. Standards were carefully weighed such that 45 mg of metal powder was transferred into each appropriate sample electrode. For all analyses, the Stallwood Jet was used with a 80:20 mixture of Ar:O₂ such that the total gas flow through the jet was 2.5 L/min. 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 6 amps, hold for 15 s, jump to 12 amps, hold for 45 s, jump to 15 amps, hold for 60 s
Analytical Gap	4 mm
Electrodes	
Sample Electrode	1/4" in diameter with an undercut cup
Counter Electrode	1/8" diameter and pointed
Sample	
Sample Size	45 mg
Internal Standard	None
Integration Time	0-120 seconds

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 with an undercut cup (part # S-4). 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 cobalt powdered metal standards that contained the analytes of interest at 0, 1, 10, 100 and 1000 ppm. Calibration standards were prepared 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.

The DC Arc Technique for Co

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 profile is shown in Figure 1. The figure is based on a time-resolved analysis (TRA) scan of a 1000 ppm multi-element standard in a cobalt metal matrix obtained over the course of a DC Arc burn that lasted 120 seconds.

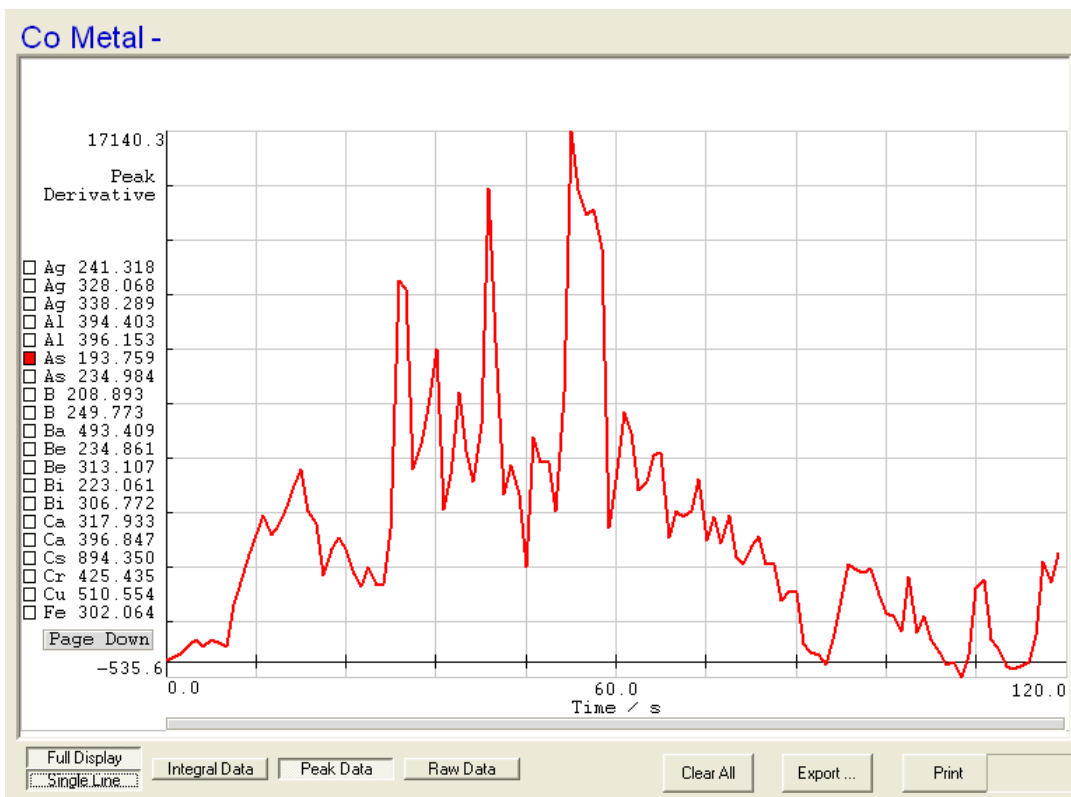


Figure 1. Time-Resolved Analysis Scan of As in the 1000 ppm Calibration Standard

In Figure 1, data for the emission of As at 193 nm is plotted as a function of time. As illustrated above, the majority of the emission from As was observed mid-way through the arc burn; however, significant measurable emission was observed over the course of the entire burn. All wavelengths were examined in this fashion and the profile illustrated in Figure 1 was observed for all analytes of interest. For this reason, individual time gates were not used and emission from all elements was collected from 0-120 seconds.

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
Ag	328.068	1	15
As	193.759	---	12
B	249.773	---	14
Ba	493.409	---	13
Be	234.861	2	---
Bi	306.772	---	15
Cr	425.435	3	---
Cs	894.350	---	15
Fe	302.064	1	---
Ga	417.206	4	---
Ge	270.963	---	13
In	410.177	---	15
K	766.491	---	15
Li	670.784	1	---
Mg	279.553	3	---
Mn	257.610	---	14
Ni	300.249	3	---
Rb	780.023	2	---
Sb	217.589	4	---
Si	251.612	2	15
Sn	283.999	2	---
Sr	421.552	---	15
Te	214.275	---	15
Ti	323.452	---	12
V	318.398	---	15
Zn	206.191	---	15

Table 2. Wavelengths and Background Correction Points 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 Ag at 328.068 nm in the 1 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 7, 8 and 9.

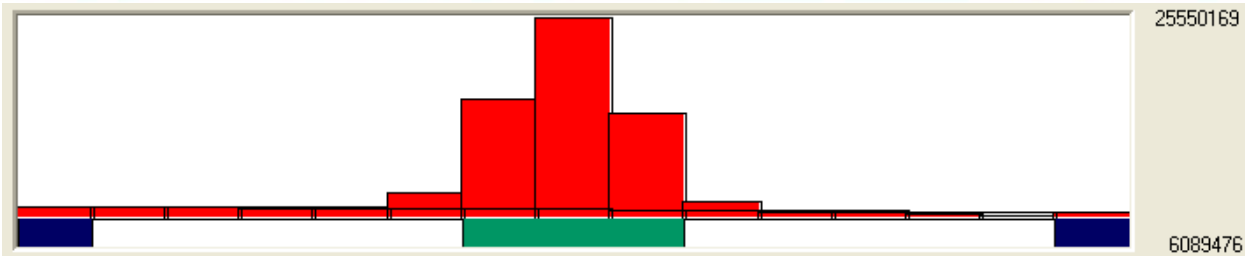


Figure 2. Graphical Representation of the Ag 328.068 nm Subarray for the 1 ppm Calibration Standard

Examples of typical calibration curves for elements measured in high purity cobalt are illustrated in Figures 3 and 4. Figures 3 and 4 contain calibration curves for As at 193.759 nm and Mg at 279.553 nm, respectively, to demonstrate typical precision and accuracy for the analytes measured in this work. As these figures indicate, the Co matrix produced significant background structure on top of the emission generated for many of the analytes of interest such that most analytes could not be calibrated to concentrations higher than 100 ppm.

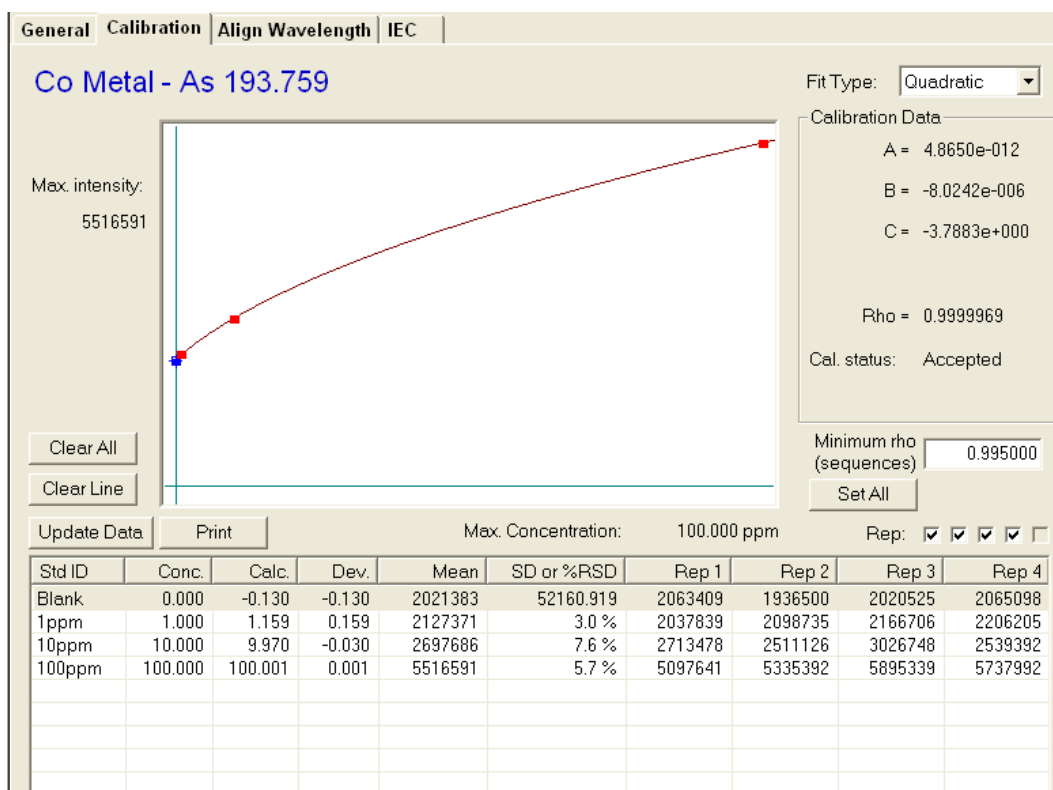


Figure 3. Calibration Curve of As at 193.759 nm in High Purity Cobalt

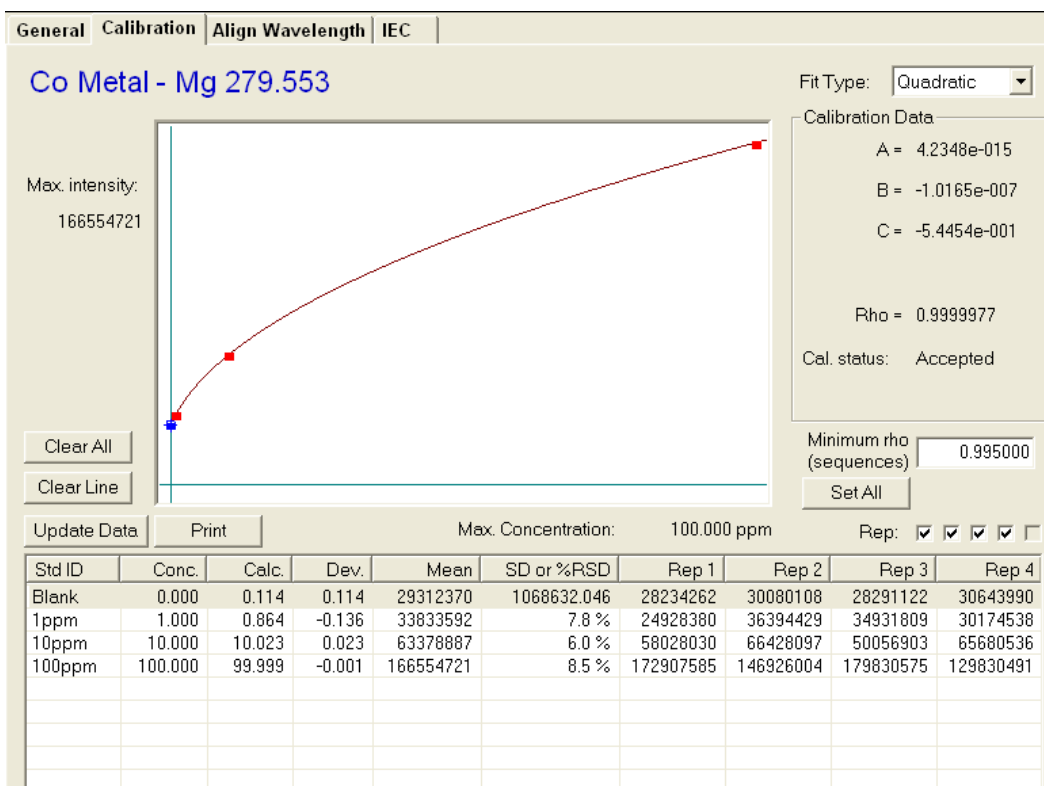


Figure 4. Calibration Curve of Mg at 279.553 nm in High Purity Cobalt

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).

Element	Wavelength (nm)	Detection Limit (ppm)
Ag	328.068	0.44
As	193.759	2.0
B	249.773	0.18
Ba	493.409	1.1
Be	234.861	0.05
Bi	306.772	0.10
Cr	425.435	3.9
Cs	894.350	0.60
Fe	302.064	2.1
Ga	417.206	2.1
Ge	270.963	0.58
In	410.177	1.8
K	766.491	2.1
Li	670.784	0.01
Mg	279.553	0.99
Mn	257.610	0.21
Ni	300.249	0.37
Rb	780.023	0.36
Sb	217.589	1.6
Si	251.612	15
Sn	283.999	0.12
Sr	421.552	2.4
Te	214.275	0.39
Ti	323.452	1.0
V	318.398	1.5
Zn	206.191	0.59

Table 3. Detection Limits in High Purity Cobalt Metal

Conclusions

The analysis of cobalt 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 cobalt metal matrix.

As indicated in Table 3, there are no detection limits reported for Al and Ca. The powdered metal used in this work contained Al and Ca impurities at high concentrations which significantly degraded the detection limits that would have been obtained in a pure metal matrix. The powdered metal also contained Ba and Mg impurities; however, they were present at trace levels and only produced slight degradations in the detection limits for those elements. It should also be noted that the detection limit for Si reflects inhomogeneties in the standards more than imprecision in the instrument.