



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

INTRODUCTION

High purity nickel is predominantly used in the production of metal alloys; however, it is also used in the production of many domestic and world-wide consumer products including rechargeable batteries, magnets, catalysts and coins, including the United States 5 cent piece. Nickel, in its powdered form, is mixed with iron or copper metal powders to increase the density of auto parts such as clutch plate holders, rotors and gears.

The analysis of nickel alloys is relatively rapid and simple when performed by DC Arc. Digestion procedures are often complex, time-consuming and increase the risk of sample contamination during preparation. Direct sample analysis eliminates the need for sample digestion and allows the nickel samples to be analyzed in their native form.

The advent of array detector technology provides significant improvements over photographic plate and PMT-based DC Arc spectrometers. Charge injection device (CID) detectors provide full wavelength coverage and offer advantages such as: simultaneous background correction, the use of multiple wavelengths per element, the ability to perform time-resolved analysis and shorter analysis times.

This application note contains preliminary data to demonstrate the ability of the Teledyne Leeman Labs Prodigy DC Arc spectrometer to determine trace elements in high purity nickel. 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 nickel.



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 format array detector, creates 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.

Operating 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 an undercut cup and a 1" post (part # L-4012). The counter electrodes were 1/8" in diameter and pointed (part # C-1 ST-21). A 2 mm analytical gap was used and the position of the electrodes was adjusted during the sample burn to maintain a distance of 2 mm between the sample and the counter electrode. All analyses were performed in air and at a constant current of 10 amps.

Calibration Standards

The instrument was calibrated with several high-purity nickel Certified Reference Materials (CRMs) that contained the analytes of interest at concentrations which ranged from 0.1 to 545 ppm. The nickel standards consisted of flat metal chips (187A, 188A, 189A, 190A and 191A) and were purchased from Analytical Reference Materials International (Golden, CO). Each standard was prepared for analysis by quantitatively transferring chips into a sample electrode such that the final mass of the standard was as close to 0.1 g as possible. The concentrations used for calibration are listed in Table 1. The calibration curves were constructed by using a least-squares regression of the CRM concentrations and the background subtracted analyte intensities ratioed to the nickel internal standard (IS) intensity.

Element	Std 187A (ppm)	Std 188A (ppm)	Std 189A (ppm)	Std 190A (ppm)	Std 191A (ppm)
Ag	0.1	1.1	2.4	10.9	0.1
Al	11	24	44	50	1.5
As	0.1	0.7	0.7	28	13
Bi		0.9	2.6	11.1	
Cd		0.2	0.8	5.0	
Co	1.0	1.7	3.1	8.0	545
Cr	3.0	6.0	10	1.0	2.1
Cu	2.2	1.8	9.0	17	4.2
Fe	19	19	38	99	7.9
Mg	2.0	4.0	8.0	6.0	2.0
Mn	3.0	2.3	1.9	1.8	3.1
Pb	0.15	1.0	2.9	9.3	0.3
Sb		1.1	3.9	11	
Se		0.7	2.1	6.5	1.9
Si		18	19	28	5.0
Sn	0.4	1.1	2.2	6.2	0.4
Te		0.8	1.7	8.9	
Zn		2.3	2.8	8.1	1.9

Table 1. 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 Zn at 213.856 nm in the 188A calibration standard which contained 2.3 ppm of Zn. In Figure 1, the left and right background correction points are illustrated in blue at pixel positions 3 and 13, respectively. Each background correction point has a width of 1 pixel. The pixels used for integrating the analytical peak are illustrated in green at positions 7, 8 and 9.

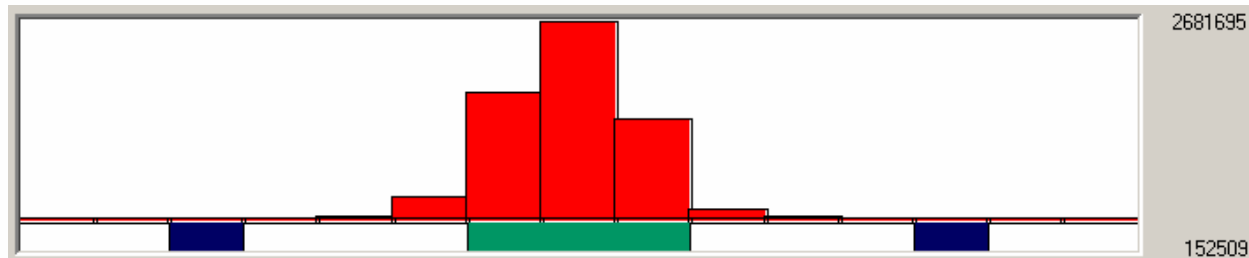


Figure 1. Graphical Representation of the Zn 213.856 nm Subarray for the 188A Calibration Standard

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 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.

Element	Wavelength (nm)	Left Background Position	Right Background Position	Integration Period (s)
Ag	328.068	---	12	0-25
Al	396.152	---	15	0-25
As	189.042	3	---	0-25
Bi	306.772	---	9	0-25
Cd	214.441	---	15	0-25
Co	228.615	1	---	0-25
Cr	284.325	1	---	0-25
Cu	324.754	3	11	0-25
Fe	248.327	1	---	0-25
Mg	279.553	4	---	0-25
Mn	257.610	---	13	0-25
Pb	283.305	---	9	0-25
Sb	217.581	6	---	0-25
Se	196.090	5	---	0-25
Si	251.432	4	---	0-25
Sn	317.505	2-3	---	0-25
Te	214.281	---	14	0-25
Zn	213.856	3	13	0-25
Ni	243.789	2-3	---	0-25

Table 2. Wavelengths, Background Correction Points and Integration Times Used

The DC Arc Technique for Ni

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. These distillation profiles can be used for choosing integration time periods that maximize the signal to noise ratio for each analyte of interest. The integration periods used for this work are listed in Table 2.

Examples of typical calibration curves for elements measured in high purity nickel are illustrated in Figures 2 and 3. Figures 2 and 3 contain calibration curves for Bi at 306.772 nm and Pb at 483.687 nm, respectively, to demonstrate typical precision and linearity for the analytes measured in this work.

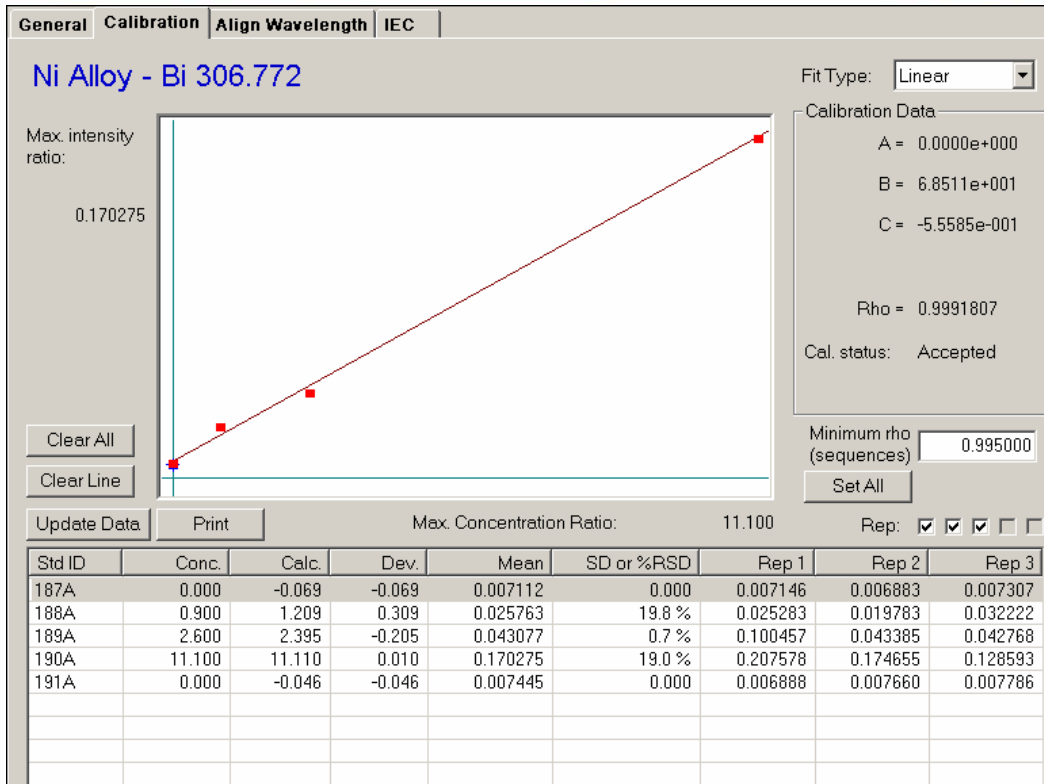


Figure 2. Calibration Curve of Bi at 306.772 nm in High Purity Ni

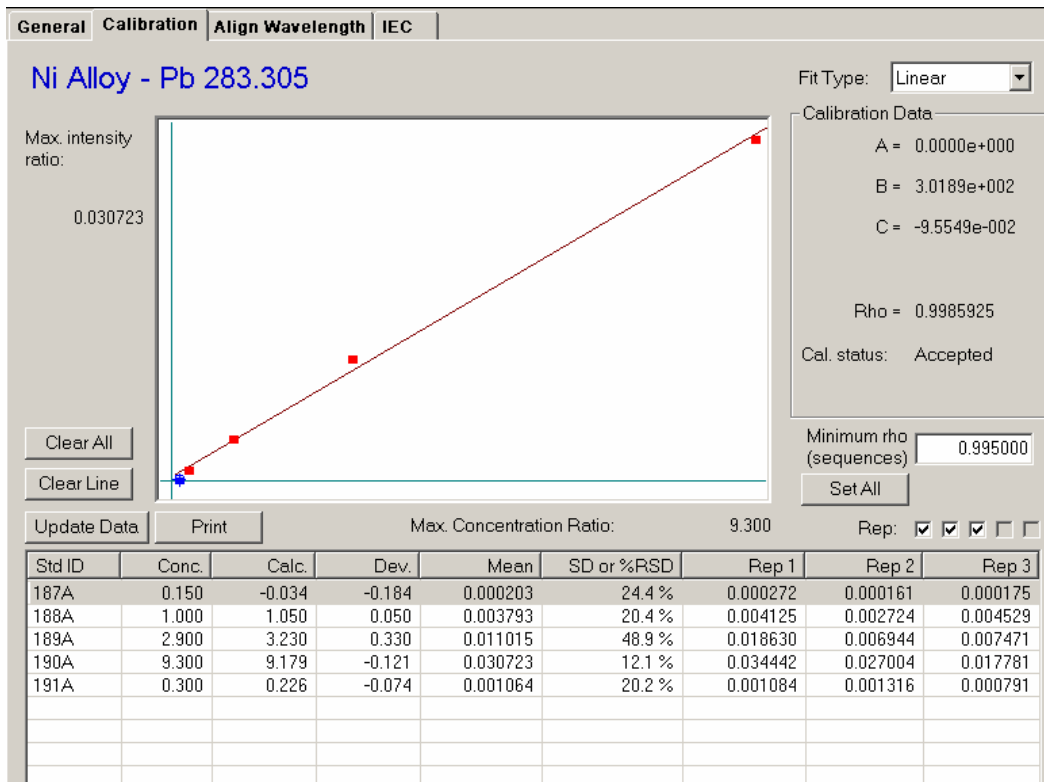


Figure 3. Calibration Curve of Pb at 283.305 nm in High Purity Ni

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 3 replicate measurements of the lowest calibration standard (187A). 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	328.068	0.11
Al	396.152	17
As	189.042	17
Bi	306.772	0.30
Cd	214.441	1.1
Co	228.615	13
Cr	284.325	2.5
Cu	324.754	8.2
Fe	248.327	14
Mg	279.553	0.36
Mn	257.610	0.69
Pb	283.305	0.50
Sb	217.581	0.23
Se	196.090	6.0
Si	251.432	24
Sn	317.505	1.1
Te	214.281	0.41
Zn	213.856	8.7


Table 3. Detection Limits in High Purity Ni

Conclusions

The preliminary analysis of high purity Ni 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 high purity nickel.

Future Work

Future work will be conducted to determine whether precision and detection limits can be further improved for elements in a high purity nickel matrix. Future investigations will include the use of current programs with higher powers to melt the Ni sample during the arc burn and increase the emission intensities for the analytes of interest.



An investigation will also be conducted to determine whether the form of the sample has an effect on the reproducibility of the arc burns and, therefore, the detection limits. The metal chips will be ground to a smaller, more uniform size to allow the arc to melt the entire sample without anchoring to one of the larger chips inside the sample electrode cup. As an alternative to grinding, the metal chips will be converted to the oxide form, ground to a fine powder, mixed with high purity graphite powder and analyzed using packed electrodes.