Analysis of Trace Elements, Including Sulfur, in Copper Using the Prodigy DC Arc Spectrometer

Introduction

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 often dilute the sample 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 and continues to be the primary technique used by manufacturers of Grade 1 cathode copper as it provides the sensitivity required for the application. DC Arc also eliminates the need for sample dissolution and greatly increases the speed with which samples are prepared and analyzed.

This application note will demonstrate the ability of the Teledyne Leeman Lab's **Prodigy DC Arc** to determine trace elements, including sulfur, in high-purity copper.

Experimental

Operating Parameters

All analyses were performed on the Teledyne Leeman Lab's **Prodigy DC Arc** in atmosphere without the use of the Stallwood Jet. Nitrogen was used to purge the optical path between the DC Arc and the spectrometer's optical entrance window to allow for the determination of sulfur.

The use of the Purged Optical Path (POP) tube is illustrated in Figure 1. The remaining instrument and method conditions used are listed in Table I.

The sample and counter electrodes were purchased from Bay Carbon Inc (Bay City, MI) and used as received. The sample electrodes used for all analyses were mushroom style electrodes (part # PD-1). The counter electrodes used were 1/8" in diameter and pointed (part # C-1). A 4 mm analytical gap was set and maintained during the sample burn.

Figure 1 POP Tube for Sulfur Analysis

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Table I DC Arc Operating Conditions	
Parameter	**Setting**
DC Arc Stand	
Current	Ignition at 6A, jump to 10.5A, hold at 10.5A for 100 s
Stallwood Jet	None
Analytical Gap	4 mm
Electrodes	
Counter Electrode	1/8” diameter and pointed (ASTM #C-1)
Sample Electrode	Mushroom style (# PD-1)
Sample	
Sample Size	250 mg +/- 20 mg
Internal Standard	None
Integration Time	0-100 s for all wavelengths

Calibration

The instrument was calibrated with two sets of high-purity copper standards that contained the analytes of interest at concentrations which ranged from 0.01 to 320.0 ppm. The first set of copper standards consisted of certified reference materials produced from unalloyed copper rods (CS001, CS005, CS010, CS030, CS050, CS100, CS200) obtained from CopperSpec (Salt Lake City, UT).

The second set of copper standards consisted of certified reference materials produced as copper rods (CS1, CS2, CS3, CS4, CS5) obtained from the Institute of Non-Ferrous Metals (Gliwice, Poland). CopperSpec standards were in the form of round discs, each weighing 250 mg, and were used as received. The standard rods from the Institute of Non-Ferrous Metals were drawn out into wire form and cut into pieces such that each piece weighed 125 mg. Two wire pieces were required for each arc burn to ensure that the data for each standard was based upon a piece of copper with a mass of 250 mg.

An example calibration curve for elements measured in high-purity Cu is illustrated in Figure 2 for Ag at 338.289 nm. The calibration curve for Ag, illustrated below, demonstrates typical precision and accuracy for the concentrations over which the instrument was calibrated.

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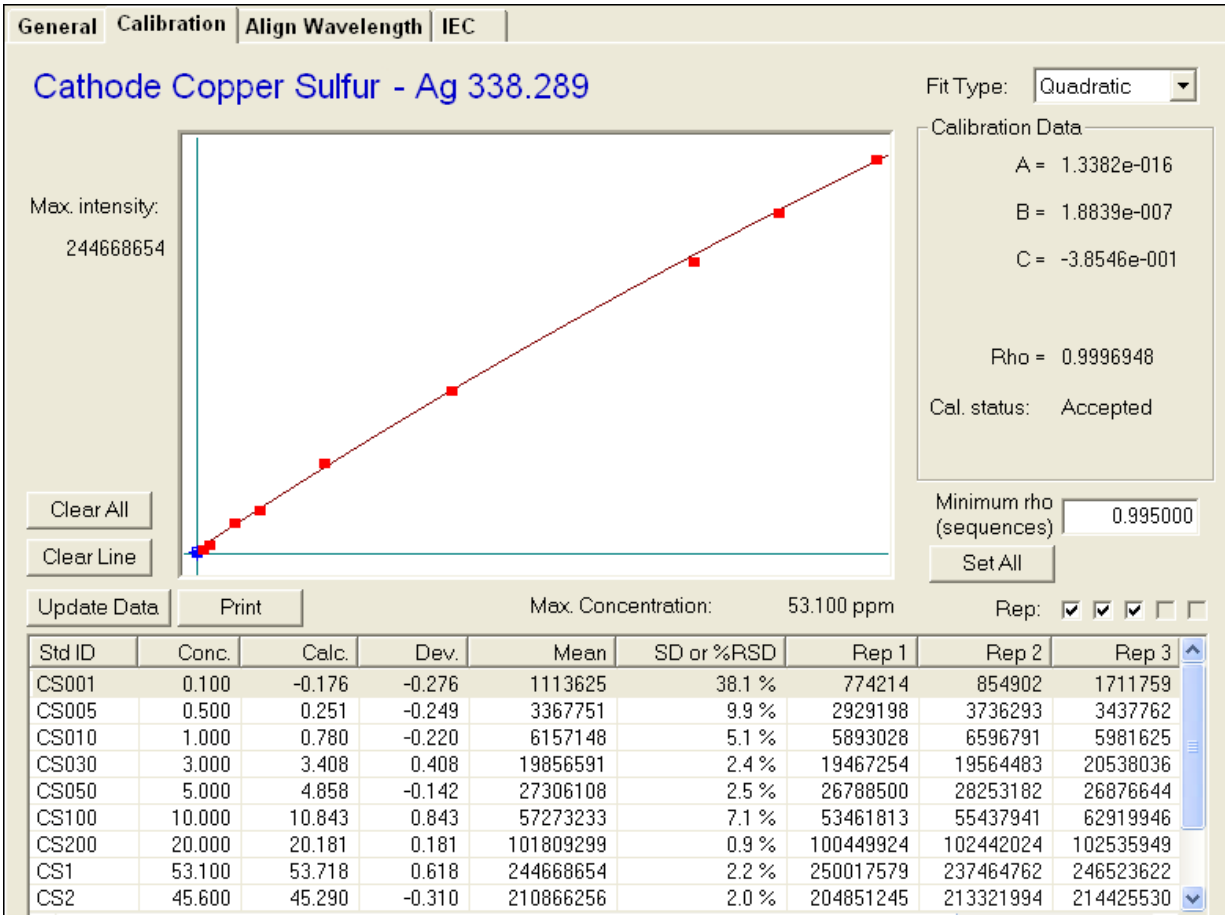
Figure 2 Calibration Curve of Ag at 338.289 nm in High Purity Copper



Std ID	Conc.	Calc.	Dev.	Mean	SD or %RSD	Rep 1	Rep 2	Rep 3
CS001	0.100	-0.176	-0.276	1113625	38.1 %	774214	854902	1711759
CS005	0.500	0.251	-0.249	3367751	9.9 %	2929198	3736293	3437762
CS010	1.000	0.780	-0.220	6157148	5.1 %	5893028	6596791	5981625
CS030	3.000	3.408	0.408	19856591	2.4 %	19467254	19564483	20538036
CS050	5.000	4.858	-0.142	27306108	2.5 %	26788500	28253182	26876644
CS100	10.000	10.843	0.843	57273233	7.1 %	53461813	55437941	62919946
CS200	20.000	20.181	0.181	101809299	0.9 %	100449924	102442024	102535949
CS1	53.100	53.718	0.618	244668654	2.2 %	250017579	237464762	246523622
CS2	45.600	45.290	-0.310	210866256	2.0 %	204851245	213321994	214425530

Results

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 CS001 high-purity copper standard. Results for the detection limit study are listed in Table II in units of parts per million (ppm).

Table II Detection Limits in High-Purity Copper Metal							
Element	Wavelength (nm)	Detection Limit (ppm)	Integration Time (s)	Element	Wavelength (nm)	Detection Limit (ppm)	Integration Time (s)
Ag	338.289	0.02	0-100	P	255.493	5.1	0-100
As	193.759	0.06	0-100	Pb	283.305	0.015	0-100
B	249.678	0.02	0-100	S	180.731	0.6	0-100
Bi	306.772	0.016	0-100	Sb	231.147	0.4	0-100
Cd	214.438	0.19	0-100	Se	203.985	0.8	0-100
Co	345.351	0.09	0-100	Si	251.612	2.7	0-100
Cr	425.435	0.02	0-100	Sn	283.999	0.05	0-100
Fe	302.064	0.09	0-100	Te	238.576	0.2	0-100
Mn	257.610	0.15	0-100	Zn	481.053	0.04	0-100
Ni	305.082	0.2	0-100				

Conclusions

The analysis of high-purity copper using the **Prodigy DC Arc** 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 that are reflected in the detection limit data. The calibration curve and detection limit data illustrate that the presence of the nitrogen purge gas allows for the measurement of sulfur; however, the presence of this gas does not affect the sensitivity or precision of the other elements in the matrix.

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