



Determination of Trace Elements in Copper by Radially Viewed Inductively Coupled Plasma Spectrometry

INTRODUCTION

Copper is considered to be the first metal used by man and has been mined for more than 10,000 years. Since copper is a soft, malleable metal, early civilizations learned to fashion tools, containers, ornaments and weapons from it. Once it was discovered that the addition of a small amount of tin to molten copper produced an alloy that was harder than copper, the Bronze Age had begun.

Today, copper and its alloys are one of the major groups of commercial metals, ranking third in world metal consumption after steel and aluminum. They are also among the most versatile engineering materials available. Copper and its alloys have a number of key properties that make them suitable for many applications. Some of these properties are:

- Excellent electrical conductivity (second only to Ag and Au)
- Excellent heat conductivity
- Good corrosion resistance
- Good machinability
- They are non-magnetic
- They retain their mechanical and electrical properties at cryogenic temperatures

These properties can be altered with variations in composition and manufacturing methods. For example, Pb and Te can be added to copper to improve machinability

Worldwide copper consumption is in the vicinity of 18 million tons per year. The largest consumer of copper is the building industry; followed by the electronics industry. The most common grade of copper is that used in standard water pipe.

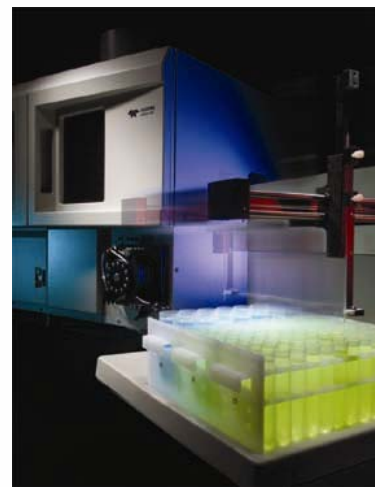
The presence of trace impurities in copper and its alloys can adversely affect the properties of finished products. For example, the presence of Fe, Pb and Sn in electrolytic copper will increase electrical resistance. Corrosion characteristics of Cu alloys can be affected by the presence of other metals above or below strictly controlled levels. As a result, the concentration of impurities must be kept under control in order to ensure the quality of the metal.

This application note will demonstrate the ability of the Teledyne Leeman Labs Prodigy High Dispersion ICP to determine trace impurities in Cu reference materials. The analytes measured in this work include: Ag, Al, As, Cd, Cr, Fe, Mg, Ni, P, Pb, Sb, Si, Sn, Mn, Co, Bi, Zn and Te.

Instrumentation

A Prodigy High Dispersion Inductively Coupled Plasma (ICP) Spectrometer equipped with a radial view torch and an 88-position autosampler was used to generate the data for this application note.

The Prodigy is a compact bench-top simultaneous ICP-OES system featuring an 800 mm focal length Echelle optical system coupled with a megapixel Large Format Programmable Array Detector (L-PAD). At 28 x 28 mm, the active area of the L-PAD is significantly larger than any other solid-state detector currently used for ICP-OES. This combination allows Prodigy to achieve significantly higher optical resolution than other solid-state detector based ICP systems. The detector also provides continuous wavelength coverage from 165 to 1100 nm permitting measurement over the entire ICP spectrum in a single reading without sacrificing wavelength range or resolution. This detector design is inherently anti-blooming and is capable of random access, non-destructive readout that results in a dynamic range of more than 6 orders of magnitude. For applications that require the measurement of chlorine, bromine or iodine an optional halogen detection system is available.



The Prodigy uses a 40.68 MHz free running, water-cooled oscillator, allowing it to handle even the most difficult sample matrices. A high sensitivity sample introduction system ensures that sufficient and steady emission signals are transmitted to the spectrometer. The torch and sample introduction system are uniquely integrated into the optical system through Prodigy's innovative Image Stabilization system, which treats the torch as an optical component by rigidly attaching it to the spectrometer.

The sample introduction system consists of a four-channel peristaltic pump, cyclonic spray chamber with a knockout tube, single piece quartz torch and a high solids concentric nebulizer. The specific operating conditions used in this work are described in **Table 1**.

Method

Sample Preparation

Two reference materials, MBH 17869N and MBH 17867P, were used in this study. Since these are chill cast discs, a lathe was used to machine off approximately 2 – 3 grams of material. Approximately 1 gram of each material was then placed in separate Teflon[®] beakers, covered with a minimum of deionized water (DIW) and placed on a hot plate. The samples were dissolved using 5 ml of nitric acid (HNO₃) added 1 ml at a time while gently heating. Once the dissolution was complete, the samples were diluted to 100ml with Deionized Water (18 megohm).

Calibration Standards

Multielement calibration standards were made from single element Teledyne Leeman Labs Plasma Pure[®] ICP standards. In addition, the standards were matrix-matched to the Cu concentration of the reference materials using Plasma Pure[®] Cu concentrate. The final acid concentration in the standards was 5% HNO₃. Analyte concentrations in the standards were 0, 5 and 10 ppm for all elements.

Instrument Operating Conditions

The Prodigy operating parameters are listed in **Table 1**.

Parameter	Setting	Part Number
RF Power	1.3 kW	
Torch Type	Radial 1 piece quartz	120-00336-3
Coolant Flow	16 l/min	
Auxiliary Flow	0 l/min	
Plasma View	Radial	
Nebulizer Pressure	34 psi	
Nebulizer Type	High Solids Concentric	120-00474-1
Spray Chamber	Cyclonic with Knockout	120-00475-1
Sample Uptake Rate	1.1 ml/min	
Optical Purge Flow	Low	
Integration Time	30 sec	

Table 1. Instrument Operating Parameters

The analytical viewing zone was set by using a 10 ppm Mn standard. The optimum viewing position is automatically selected by the Prodigy's software.

Wavelength Parameters

For each wavelength, **Prodigy** uses a 3 x 15 pixel subarray, which is typically centered on the wavelength of interest. Background correction points and the analytical peak have both position and width values within the subarray. In **Table 2**, the position value is designated by "x" in the column header, while "w" indicates the width. The default position for the analytical peak is 7 with a width of 3 pixels. Where possible, two wavelengths were used for each element. All data in the subarrays are collected simultaneously. In addition, all pixel data are saved, permitting recalculation of results at a later time.

	LBX	LBW	Peak X	Peak W	RBG X	LBG W
Ag 328.068 r	3	1	7	3	14	2
Ag 338.289 r	6	1	7	3	12	2
Al 396.152 r	3	3	7	3	12	2
Al 308.215 r	5	1	7	3	11	1
As 189.042 r	1	3	7	3	13	3
As 193.759 r	1	0	7	3	12	3
Cd 214.441 r	1	3	7	3	13	3
Cd 226.502 r	3	2	7	3	12	2
Cr 267.716 r	1	3	7	3	13	3
Fe 259.940 r	3	2	7	3	12	2
Fe 238.204 r	1	1	7	3	14	2
Mg 279.553 r	1	3	7	3	13	3
Mg 285.213 r	5	1	7	3	13	3
Ni 231.604 r	4	0	7	3	13	3
Ni 221.648 r	6	1	7	3	10	1
P 185.941 r	3	2	7	3	15	0
P 178.283 r	3	3	7	3	12	2
Pb 220.353 r	6	1	7	3	10	1
Pb 217.000 r	6	1	7	3	10	1
Sb 206.833 r	3	2	7	3	12	0
Sb 217.581 r	6	1	7	3	10	1
Si 288.158 r	3	2	7	3	12	0
Si 251.611 r	1	3	7	3	13	1
Sn 189.991 r	2	2	7	3	13	3
Sn 224.605 r	6	1	8	3	10	1
Mn 257.610 r	1	3	7	3	14	2
Mn 259.372 r	1	2	7	3	14	2
Co 228.615 r	1	3	7	3	13	2
Co 236.379 r	4	2	7	3	12	2
Bi 223.061 r	6	0	7	3	11	1
Bi 306.772 r	5	1	7	3	13	1
Zn 206.200 r	5	1	7	3	11	3
Te 214.281 r	6	1	7	3	10	1
Te 238.578 r	3	3	7	3	11	1

Table 2. Wavelength Parameters

As an example, **Figure 1** illustrates the element parameter for the As 189.042 nm line. In the figure, the left and right background regions begin at pixel positions 1 and 13, respectively, with widths of 3 pixels. The analytical region of interest, where the As peak is found, begins at pixel position 7 and has a width of 3 pixels. The thin line running under the peak shows the calculated background correction based on the two correction regions.



Figure 1. As 189.042 nm Element Parameter Example

Figure 2 illustrates a calibration curve showing typical precision and linearity for the concentration range used.

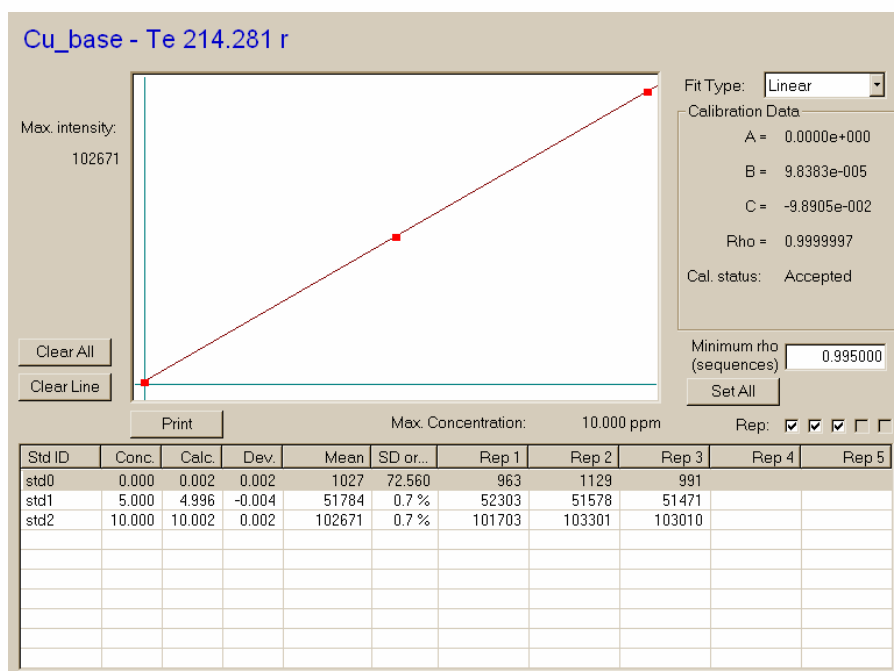


Figure 2. Typical Calibration Curve

Results

After igniting the plasma and allowing a 15 minute warm-up period, the Prodigy was calibrated using the 88-position autosampler. Once the calibration was complete, a 1 ppm QC Standard was analyzed with an acceptance criteria of $\pm 10\%$. Upon successful completion of the QC Standard analysis, the reference samples were analyzed. After the sample analysis, the QC Standard was re-analyzed. (The Prodigy's software allows the entire sequence to be run unattended. Should a QC Standard be out of specification, the Prodigy automatically allows a variety of actions, including recalibrating and rerunning the QC Standard and any samples that were analyzed since the last successful QC Standard was run.)

The analysis results are shown in **Table 3**. All concentrations are in “%”. The values measured by the Prodigy are contained in the column labeled “Found %” while the certified values are in the column labeled “Certified %”. The agreement between the measured and certified values is quite good.

Element	MBH17867P		MBH17869N	
	Found %	Certified %	Found %	Certified %
Ag 328.068 r	0.010	0.011±0.001	0.034	0.033
Ag 338.289 r	0.011		0.035	
Al 396.152 r	ND	-	0.11	0.10
Al 308.215 r	ND		0.11	
As 189.042 r	0.030	0.027±0.004	0.007	0.008
As 193.759 r	0.030		0.007	
Cd 214.441 r	0.022	0.020	0.006	0.007
Cd 226.502 r	0.021		0.007	
Cr 267.716 r	0.009	0.010±0.002	0.006	0.007
Fe 259.940 r	0.009	0.010±0.001	0.034	0.034
Fe 238.204 r	0.009		0.034	
Mg 279.553 r	ND	-	0.042	0.038
Mg 285.213 r	ND	-	0.043	
Ni 231.604 r	0.042	0.040	0.010	0.011
Ni 221.648 r	0.046		0.010	
P 185.941 r	0.007	0.009±0.001	0.028	0.034
P 178.283 r	0.006		0.032	
Pb 220.353 r	0.008	0.009	0.031	0.029
Pb 217.000 r	0.007		0.033	
Sb 206.833 r	0.014	0.014	0.015	0.020
Sb 217.581 r	0.014		0.016	
Si 288.158 r	ND	<0.003	0.009	0.012
Si 251.611 r	ND		0.009	
Sn 189.991 r	0.034	0.033±0.001	0.008	0.011
Sn 224.605 r	0.036		0.013	
Mn 257.610 r	0.001	0.002	0.023	0.022
Mn 259.372 r	0.001		0.023	
Co 228.615 r	0.028	0.027±0.002	0.007	0.007
Co 236.379 r	0.028		0.007	
Bi 223.061 r	0.005	0.008	0.024	0.034
Bi 306.772 r	0.008		0.029	
Zn 206.200 r	0.036	0.037±0.004	0.010	0.011
Te 214.281 r	0.008	0.009	0.030	0.030
Te 238.578 r	0.009		0.029	

Table 3. Reference Sample Results, %

Using the 1% Cu calibration blank, detection limits for all the wavelengths used were determined. The detection limits were calculated by analyzing the calibration blank 10 times and multiplying the resulting Standard Deviation by 3. The Detection Limits are given in **Table 4**.

Line	DL, ppm Solid	Line	DL, ppm Solid
Ag 328.068 r	0.48	Mn 257.610 r	0.02
Ag 338.289 r	0.44	Mn 259.372 r	0.06
Al 308.215 r	2.51	Ni 221.648 r	2.37
Al 396.152 r	0.76	Ni 231.604 r	0.66
As 189.042 r	4.63	P 178.283 r	6.02
As 193.759 r	2.37	P 185.941 r	9.04
Bi 223.061 r	18.1	Pb 217.000 r	35.9
Bi 306.772 r	4.98	Pb 220.353 r	8.87
Cd 214.441 r	0.19	Sb 206.833 r	4.38
Cd 226.502 r	0.12	Sb 217.581 r	14
Co 228.615 r	0.37	Si 251.611 r	0.92
Co 236.379 r	0.53	Si 288.158 r	0.89
Cr 267.716 r	0.14	Sn 189.991 r	1.53
Fe 238.204 r	0.15	Sn 224.605 r	33.3
Fe 259.940 r	0.12	Te 214.281 r	10.2
Mg 279.553 r	0.02	Te 238.578 r	10.2
Mg 285.213 r	0.08	Zn 206.200 r	0.27

Table 4. 3σ Detection Limits.

Conclusion

The analysis of residual elements in copper has been carried out for 18 elements using a radially viewed Teledyne Leeman Labs, Prodigy High Dispersion ICP. Accurate results were obtained by carefully matrix matching the base copper concentration of the samples to the calibration standards.

The sample introduction system performed without any clogging of the torch or nebulizer and did not require the use of an argon humidifier.

The image stabilized plasma and the simultaneous data collection of both peak and background data combine to provide exceptionally precise and stable results.