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TECHNOLOGY:	ICP
INDUSTRY:	QA/QC

Determination of Trace Elements in Copper (Cu) Using the Teledyne Leeman Labs' Radial View ProdigyPlus ICP-OES

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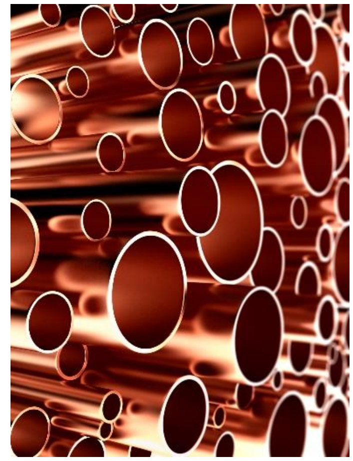
Introduction



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

Today, Cu and its alloys are one of the major groups of commercial metals, ranking third in world metal consumption, after steel and aluminum. Worldwide Cu consumption is roughly 23.8 million metric tons per year with the largest consumers being the building and electronics industries.

Among the most versatile engineering materials available, Cu and Cu alloys have several key properties that make them suitable for numerous applications:

- Excellent electrical conductivity, second only to silver (Ag)
- Excellent heat conductivity
- Good corrosion resistance
- Good machinability
- Non-magnetic
- Retention of mechanical and electrical properties at cryogenic temperatures

The properties of Cu and Cu alloys can be enhanced by variations in composition and manufacturing methods. For example, lead (Pb) and tellurium (Te) can be added to Cu to improve machinability. Conversely, the presence of trace impurities in Cu and Cu alloys can adversely affect the properties of finished products. The presence of iron (Fe), lead (Pb) and tin (Sn) in electrolytic Cu will increase electrical resistance. Corrosion characteristics of Cu alloys can also be affected by the presence of metals above or below performance specifications. As a result, the concentration of impurities must be monitored to ensure the quality of the metal.

This application note will demonstrate the ability of the Teledyne Leeman Labs' ProdigyPlus High-Dispersion ICP to determine trace impurities in Cu reference materials.

Instrumentation

A ProdigyPlus High-Dispersion ICP-OES system equipped with a radially viewed torch and a 120-position CETAC ASX-280 autosampler (Figure 1) were used to generate the data for this application note.

Figure 1 ProdigyPlus ICP-OES and ASX-280 Autosampler

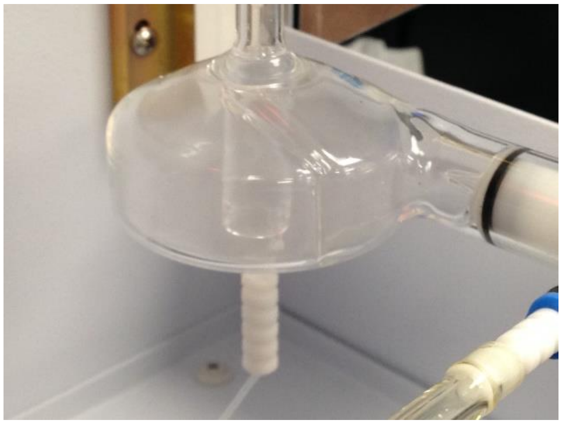
The ProdigyPlus is a compact benchtop simultaneous ICP-OES system featuring an 800 mm focal length Echelle optical system coupled with a mega-pixel large format CMOS detector. At 28 x 28 mm, the active area of the CMOS detector is significantly larger than any other solid-state detector currently used for ICP-OES. This combination allows the ProdigyPlus to achieve higher optical resolution and dispersion than any 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. The detector design is inherently anti-blooming and is capable of random access, non-destructive readout that results in a dynamic range of more than six orders of magnitude. The ProdigyPlus uses a 40.68 MHz rugged, free-running RF generator, allowing it to handle the most difficult sample matrices, as well as common organic solvents.

Sample Introduction

A high-sensitivity sample introduction system ensured that sufficient and steady emission signals were delivered to the spectrometer. The sample introduction system consisted of:

- Cyclonic spray chamber with a center knockout tube
- Conikal™ Nebulizer
- Four-Channel Peristaltic Pump

Figure 2 Cyclonic Spray Chamber with Conikal Nebulizer



The volume of the cyclonic spray chamber is low allowing for fast washout between samples, while its knockout tube efficiently reduces the amount of sample aerosol that reaches the plasma. The ProdigyPlus torch is mounted using an innovative twist-lock auto-aligning sample introduction system, shown in Figure 3. This design permits operators to remove and replace the torch to the exact same position, providing day-to-day reproducibility and simplified training. Additionally, the twist-lock design automatically connects the coolant and auxiliary gas flows, eliminating potential errors.

Figure 3 Radial Twist Lock Sample Introduction System

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 sample was placed in separate PTFE 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 (HNO_3), added 1 mL at a time, while gently heating. Once the dissolution was complete, the samples were diluted to 100 mL with DIW (18 M Ω).

Calibration Standards

Multi-element calibration standards were made from LGC single and multi-element ICP standards. The standards were matrix matched to the Cu concentration using high-purity Cu powder. The final acid concentration in the standards was 5% HNO_3. Analyte concentrations in the calibration standards were 0, 1, 5 and 10 ppm for all elements.

Instrument Operating Parameters

The ProdigyPlus instrument operating parameters are shown in Table I.

Table I Instrument Operating Conditions		
Parameter	**Value**	**Part Number**
RF Power	1.2 kW	-
Coolant Flow	14 L/min	-
Auxiliary Flow	0.3 L/min	-
Nebulizer Pressure	36 psi	-
Pump Rate	30 RPM	-
Torch	Demountable Quartz	318-00167-1
Injector	2.5 mm Quartz	318-00161-AQ1
Nebulizer	Conikal	120-00463-1
Sample Uptake Tubing	Black/Black Tab	309-00069-8
Sample Drain Tubing	Red/Red Tab	309-00063-5
Integration Time	15 s	-
Optical Purge Rate	0.7 L/min	-

The analytical viewing zone in the plasma was set using a 10 ppm manganese (Mn) standard. The optimum viewing position is automatically determined by the ProdigyPlus Salsa software by scanning the plasma horizontally and vertically to maximize intensity.

Results

After igniting the plasma and allowing a 15-minute warm-up period, the ProdigyPlus and ASX-280 autosampler ran an unattended sequence consisting of the following:

- Multi-element calibration standards in concentrations of 0, 1, 5 and 10 ppm
- 1 ppm Quality Control (QC) standard with an acceptance criteria of ±10%
- MBH 17869N and MBH 17867P reference samples
- Re-analysis of the 1 ppm QC standard with an acceptance criteria of ±10%

Should a QC standard be out of specification, the Salsa software will automatically recalibrate and rerun the QC standard and any samples that were analyzed since the last successful QC standard was run.

Results of the analysis are shown in Table II. All concentrations are shown in "%". The values measured by the ProdigyPlus are shown in the column labeled "Found %" while the certified values are shown in the column labeled "Certified %". The agreement between the measured and certified values was quite good.

Table II Analytical Results				
	MBH17867P		MBH17869N	
Element	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	0.021	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	-	0.039	0.038
Mg 285.213 r	ND	-	0.038	
Ni 231.604 r	0.039	0.040	0.010	0.011
Ni 221.648 r	0.041		0.010	
P 185.941 r	0.007	0.009±0.001	0.033	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		0.029	
Sb 206.833 r	0.014	0.014	0.017	0.020
Sb 217.581 r	0.014		0.017	
Si 288.158 r	ND	<0.003	0.010	0.012
Si 251.611 r	ND		0.009	
Sn 189.991 r	0.031	0.033±0.001	0.008	0.011
Sn 224.605 r	0.032		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	0.007	0.008	0.029	0.034
Bi 306.772 r	0.008		0.032	
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	

Using the 1% Cu calibration blank, detection limits for all wavelengths used was 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 III.

Table III 3σ Detection Limits

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

Conclusion

The analysis of residual elements in Cu was successfully carried out using a Teledyne Leeman Labs ProdigyPlus High-Dispersion ICP with radially-viewed plasma. Accurate results were obtained by careful matrix matching of the base Cu concentration of the samples to the calibration standards.

The sample introduction system performed well without any clogging of the torch or nebulizer and did not require the use of an argon humidifier. The twist-lock auto-aligning sample introduction system allowed the operator to easily remove and replace the torch in the correct position, regardless of experience, and resulted in enhanced reproducibility. The analytical results demonstrate that the ProdigyPlus is well-suited for accurate and cost-effective determination of trace elements in Cu.