



Challenge

Determination of trace element impurities in high purity copper metal

Solution

Simple nitric acid digestion followed by analysis on the high-sensitivity PlasmaQuant MS Elite

Determination of Trace Elements in Copper by ICP-MS

Introduction

High purity copper is an excellent conductor of electricity and is commonly used to make electrical equipment, although small amounts of impurities can significantly reduce the conductivity. Electrical cables are made from pure copper as they must carry electricity for many kilometers through high-voltage transmission lines.

The characteristics of pure copper metal are high ductility, high electrical and thermal conductivity, high impact strength, good creep (deformation) resistance under heat or mechanical stress, easy to weld and has low relative volatility under high vacuum due to low oxygen content.

High purity copper is produced via electrolysis, where less pure, anodic copper refined from concentrating and smelting copper ore minerals, is reduced to better than 99.99% copper at the cathode.

ICP-MS offers the capability to reach sub microgram per kilogram (ppb) detection limits making it an ideal tool for quantitative measurement of impurities in pure metals such as copper. The high-sensitivity PlasmaQuant MS Elite model, achieving in excess of 1.5 million counts per second per ppb on the Indium 115 isotope, was used in the analysis of high purity copper metal samples and standard reference materials.

Materials and Methods

Samples and Reagents

The following high purity reagents were used for solution preparations:

- Deionized water (>18.2 MΩ.cm, Millipore MiliQ)
- Nitric acid supra-quality 69 % (ROTIPURAN® Supra)
- 3 unknown pure copper samples labeled AM-1.1, AM-2.1 and AM-3.1
- Bundesanstalt für Materialforschung, Reference Material BAM-M382 Pure Copper

Calibration Standards

Calibration solutions covering the range from 0 to 500 µg/L were prepared from ICP-MS grade multi-element standards in 1% HNO₃. Internal standard solution was added online via a Y-piece with the analyte isotopes ⁴⁵Sc, ⁸⁹Y and ¹⁹³Ir at a concentration of 20 µg/L.

Sample Preparation

The samples were digested in an open vessel by accurately weighing approximately 1 g of sample material in 10 mL of Suprapur 69 % nitric acid. After complete digestion, the vessels were filled to 50.00 mL. Samples were prepared in duplicate and further diluted 20 fold in high purity water prior to analysis on the PlasmaQuant® MS Elite ICP-MS.

Instrumentation

Table 1: PlasmaQuant MS operating conditions

Parameter	Settings
Plasma gas flow	7.50 L/min
Auxillary gas flow	1.10 L/min
Nebulizer gas flow	1.03 L/min
RF power	1.25 kW
Pump rate	13 rpm
Stabilization delay	20 s
Dwell time	10,000 µs
No.of replicates	5
Scan per replicate	10
Ion Optics	Auto-optimized
Nebulizer type	Micromist™ 0.4 mL/min
Spraychamber type	Scott spraychamber
Spray chamber temperature	3 °C
Plasma torch	One-piece, quartz torch with 2.4mm injector
iCRC gas modes	Hydrogen (H ₂) - for ⁵⁷ Fe, ⁷⁵ As, ⁷⁸ Se Helium (He) - ⁵² Cr, ⁵⁵ Mn, ⁵⁹ Co, ⁶⁰ Ni, ⁶⁶ Zn None - ¹⁰⁷ Ag, ¹¹⁴ Cd, ¹¹⁸ Sn, ¹²¹ Sb, ¹²⁵ Te, ²⁰⁶⁻²⁰⁸ Pb, ²⁰⁹ Bi
Internal Standard Elements	⁴⁵ Sc, ⁸⁹ Y, ¹⁹³ Ir
Autosampler model	ASPQ 3300

Results and Discussion

According to the potential argon and matrix based interferences on certain mass/charge ratios, some isotopes were measured using collision and reaction gases via the iCRC technology. Three condition sets (H₂, He and None) as defined in Table 1 and 2 were used to provide interference-free analysis of each sample. No spectroscopic interferences, including oxide or doubly-charged ions produced by the copper matrix were anticipated on any of the analyte isotopes to be measured.

Table 2: Potential interferences and used iCRC gases

Element	Potential interference	iCRC mode	Element	Potential interference	iCRC mode
⁵² Cr	⁴⁰ Ar ¹² C, ³⁶ Ar ¹⁶ O	He	¹⁰⁷ Ag	-	no gas
⁵⁵ Mn	³⁹ K ¹⁶ O, ⁴¹ K ¹⁴ N	He	¹¹⁴ Cd	-	no gas
⁵⁷ Fe	⁴⁰ Ar ¹⁷ O, ⁴¹ K ¹⁶ O	H ₂	¹¹⁸ Sn	-	no gas
⁵⁹ Co	⁴³ Ca ¹⁶ O	He	¹²¹ Sb	-	no gas
⁶⁰ Ni	⁴⁴ Ca ¹⁶ O	He	¹²⁵ Te	-	no gas
⁶⁶ Zn	²⁶ Mg ⁴⁰ Ar, ³⁴ S ¹⁶ O ₂	He	²⁰⁶⁻⁸ Pb	-	no gas
⁷⁵ As	³⁵ Cl ⁴⁰ Ar	H ₂	²⁰⁹ Bi	-	no gas
⁷⁸ Se	³⁸ Ar ⁴⁰ Ar	H ₂			

The average results of elemental impurities in three unknown copper metal samples and a pure copper reference material are listed below in Table 3. The recovery for each analyte in the BAM M382 reference material were within $\pm 10\%$ of the certified values, while the relative standard deviation of the duplicate sample measurements were below 5 %, demonstrating the robustness of the method. The abundance sensitivity performance of the PlasmaQuant MS Elite is also demonstrated with excellent recovery observed on ⁶⁶Zn, an isotope directly adjacent to the intense ⁶⁵Cu signal resulting from the high copper matrix.

Table 3: Average results of duplicate measurements of digested pure copper samples.

Element	AM-1.1 (mg/kg)	AM-2.1 (mg/kg)	AM-3.1 (mg/kg)	BAM M382 (mg/kg)	BAM M382 Certified Values (mg/kg)
⁵² Cr	0.13	1.07	6.57	0.61	0.56 \pm 0.06
⁵⁵ Mn	0.22	1.18	6.65	0.76	0.76 \pm 0.06
⁵⁷ Fe	Not detected	12.04	31.30	6.23	6.0 \pm 0.4
⁵⁹ Co	0.033	1.22	3.55	0.72	0.73 \pm 0.07
⁶⁰ Ni	0.62	3.23	5.47	1.66	1.7 \pm 0.2
⁶⁶ Zn	5.01	7.44	11.97	6.25	6.0 \pm 0.5
⁷⁵ As	0.061	1.65	5.21	0.66	0.6 \pm 0.2
⁷⁸ Se	Not detected	0.75	3.20	0.64	0.6 \pm 0.1
¹⁰⁷ Ag	0.10	4.52	10.10	1.84	1.8 \pm 0.2
¹¹⁴ Cd	0.12	1.40	4.22	0.90	0.90 \pm 0.09
¹¹⁸ Sn	3.71	4.84	9.76	4.40	4.29 \pm 0.21
¹²¹ Sb	0.21	1.18	9.50	0.80	0.7 \pm 0.2
¹²⁵ Te	0.37	1.20	6.22	0.68	0.61 \pm 0.06
²⁰⁶⁻⁸ Pb	0.52	1.42	5.91	1.12	1.0 \pm 0.2
²⁰⁹ Bi	0.03	1.14	3.79	0.56	0.53 \pm 0.03

Conclusion

A simple and robust method was developed for the preparation and determination of impurities in high purity copper samples. The analysis of a certified reference material was performed to validate the accuracy and precision of the method. The PlasmaQuant MS Elite was the instrument of choice due to its superior sensitivity, allowing for the lowest possible detection limits to be achieved. This is particularly important given impurities in high purity metals will always be present at ultra-trace levels in the parts-per-billion and lower range.

Of particular note is that the full suite of elemental impurities in a high copper matrix were measured interference-free in <3 minutes and using only half the argon gas of competitive systems at <10 L/min. This capability greatly reduces running costs and is the result of a new and innovative Eco Plasma RF generator design available on the PlasmaQuant MS series.

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Version: 1.0
en · 12/2020

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