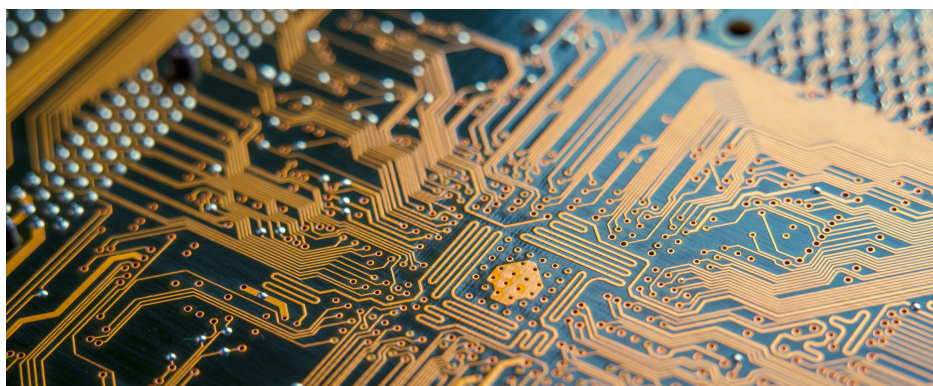Agilent

Trusted Answers

Analysis of Ultratrace Impurities in High Purity Copper using the Agilent 8900 ICP-QQQ

Low-ppt determination of alkali metals in high matrix samples using the optional "m-lens"

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Introduction

Metals such as copper (Cu), aluminum (Al), tantalum (Ta), tungsten (W), and hafnium (Hf) are essential for the manufacture of semiconductor devices. Metal sputtering targets are used to form conducting or insulating (dielectric) layers by thin film deposition using chemical vapor deposition (CVD) or physical vapor deposition (PVD). Conducting metals, originally Al but now typically Cu, are used as interconnects within wiring levels and as "vias" between layers. A complex, large-scale integrated circuit (IC) microprocessor chip may contain tens of layers of interconnect "wires" with a total length up to about 100 km *(1, 2)*. To ensure high performance and high production-yield of the final devices, very high purity metals are required for these components.

Semiconductor manufacturers may require high-purity, electronic-grade metals at grades of 5N (5 9s – 99.999% purity) up to 9N (99.9999999% purity) or above, depending on the proposed application. A 6N metal (99.9999% purity) contains a total of only 1 mg/kg (ppm) of the impurities of interest, so each individual impurity element would typically be certified as <0.01 or <0.005 ppm in the solid metal.

Determination of trace contaminants in high-purity metals is often performed using glow discharge mass spectrometry (GD-MS). However, GD-MS is expensive and requires the availability of solid metal calibration standards containing the trace elements of interest. GD-MS also has relatively slow speed of data acquisition leading to low sample throughput—around 10 minutes or more per sample—often longer when a cryo-cooled source is used. The fact that solid samples are analyzed also makes automation of sample changeover for unattended analysis more problematic than for liquid sample digests.

ICP-MS is widely used for quality-control of semiconductor materials, but some elements are difficult to measure at ultratrace levels in the presence of a high matrix. ICP-MS operating with a "cool" or reduced-energy plasma has been widely employed since the 1990s as a powerful mode for the analysis of high-purity chemicals and materials. Cool plasma suppresses the formation of intense argon-based interferences such as Ar^+ and ArO^+, allowing low-level analysis of ^{40}Ca and ^{56}Fe, respectively. Cool plasma conditions are also beneficial in the analysis of the alkali metal elements, providing lower background equivalent concentrations (BECs) than hot plasma conditions. A lower-temperature plasma causes less re-ionization of traces of easily-ionized elements (EIEs) from the cones and ion lens, giving lower background signals for these elements. Cool plasma is not universally applicable, though, as the lower power plasma has less energy, which reduces its ability to decompose the sample matrix. Poor tolerance of high matrix levels is especially problematic for the analysis of high matrix, high-purity samples such as electronic-grade metals.

This note describes a new approach to the measurement of ultratrace impurities in high-purity copper using triple quadrupole ICP-MS (ICP-QQQ). An optional ion lens (called the "m-lens") has been developed for the Agilent 8900 ICP-QQQ to allow ultra-low-level measurement of alkali metals under matrix tolerant, high-power plasma conditions. The m-lens has an optimized geometry that minimizes background signals from EIEs deposited on the ICP-MS interface components.

Experimental

Sample preparation

All samples and standards were prepared in 5% semiconductor grade TAMAPURE AA-100 nitric acid (HNO_3) bought from Tama Chemicals Co. Ltd, Kanagawa, Japan. Solutions were prepared and analyzed in PFA vials, which were cleaned with diluted HCl and HNO_3 and then rinsed using ultrapure water (UPW) before use.

A 0.1% copper (Cu) solution was prepared for analysis. A sample of 9N high purity copper was cleaned in diluted HNO_3, rinsed with UPW, weighed (about 0.05 g), and dissolved in 5 mL of 50% HNO_3 (1:1 concentrated HNO_3:UPW). The solution was brought up to volume (50 mL) with UPW, giving a total dilution of 1000x, and a matrix level of 0.1%. The 8900 ICP-QQQ can tolerate % levels of dissolved solids, but higher dilutions allow non-matrix-matched calibrations to be used. This removes the need for certified metal standards containing every element of interest. The exceptionally low detection limits of the 8900 ICP-QQQ (sub-ppt for most elements) enable ultratrace analysis even in higher sample dilutions.

The 1000x dilution factor simplifies conversion of the measured concentrations in ng/L (ppt) in the digest solution to the concentrations in µg/kg (ppb) in the original solid.

Calibration standards for 49 elements were prepared from several mixed, multi-element stock standards (SPEX CertiPrep, NJ, USA). To minimize signal suppression due to physical sample transport and nebulization effects, the calibration standards were matrix matched to the HNO_3 concentration (5%) of the Cu sample digest.

All samples and standards were spiked with a mix of three internal standard (ISTD) elements, Be, Sc, and In, at 5.0, 0.5, and 0.5 ppb, respectively. ISTDs were added to compensate for matrix differences between the standards (no Cu) and the 0.1% Cu solutions, and to correct for any long-term signal drift.

Instrumentation

An Agilent 8900 Semiconductor configuration ICP-QQQ was used for all measurements. The standard PFA nebulizer was used in self-aspiration mode, connected to the standard quartz spray chamber and quartz torch with 2.5 mm i.d. injector. The 8900 ICP-QQQ was fitted with the standard Pt-tipped sampling cone, optional m-lens (part number G3666-67500), and optional Pt-tipped, Ni-based skimmer cone for m-lens (part number G3666-67501). The skimmer cone for m-lens also requires a non-standard skimmer cone base (part number G3666-60401).

Tuning and method

Hot plasma conditions (1% CeO^+/Ce^+) were used to ensure good tolerance of the high concentration of Cu matrix. A single collision/reaction cell (CRC) tuning mode was used to measure all 49 analyte elements in the Cu samples. A cell gas mixture of oxygen (O_2) and hydrogen (H_2) was used to remove interferences using a combination of MS/MS on-mass and mass-shift modes. Operating conditions are summarized in Table 1, and acquisition parameters and given in Table 2.

Table 1. ICP-QQQ operating conditions.

Parameter	Setting
RF power (W)	1550
Sampling depth (mm)	8.0
Carrier gas flow rate (L/min)	0.70
Make-up gas flow rate (L/min)	0.46
Extract 1 (V)	0.0
Extract 2 (V)	-70
Omega bias (V)	-60
Omega lens (V)	8.0
Cell gas flow rate (mL/min)	O_2 = 0.2; H_2 = 7.0
Octopole bias (V)	-10
KED (V)	-10
Axial acceleration (V)	+2.0

Table 2. Acquisition parameters.

Element	Q1/Q2	Main interferences	Scan method	Measured ion	Integration time (s)	ISTD
Li	7/7		On-mass	Li^+	0.5	Be
B	11/11		On-mass	B^+	2.0	Be
Na	23/23		On-mass	Na^+	0.5	Sc
Mg	24/24		On-mass	Mg^+	0.5	Sc
Al	27/27		On-mass	Al^+	0.3	Sc
Si	28/28	N_2^+, CO^+	On-mass	Si^+	0.5	Sc
P	31/47	NOH^+, Cu^{++}	Mass shift	PO^+	2.0	Be
S	32/48	O_2^+, Cu^{++}	Mass shift	SO^+	2.0	Be
K	39/39	ArH^+	On-mass	K^+	0.5	Be
Ca	40/40	Ar^+	On-mass	Ca^+	0.3	Sc
Ti	48/48	SO^+	On-mass	Ti^+	0.5	Sc
V	51/51	(ClO^+)	On-mass	V^+	0.3	Sc
Cr	52/52	ArC^+	On-mass	Cr^+	0.3	Sc
Mn	55/55	$ArNH^+$	On-mass	Mn^+	0.3	Sc
Fe	56/56	ArO^+	On-mass	Fe^+	0.3	Sc
Co	59/59		On-mass	Co^+	0.3	Sc
Ni	60/60		On-mass	Ni^+	0.5	Sc
Zn	68/68	$ArNN^+$, $CuHHH^+$	On-mass	Zn^+	2.0	Sc
Ga	71/71		On-mass	Ga^+	0.5	In
Ge	72/72	$ArAr^+$	On-mass	Ge^+	0.5	In
As	75/91	$(ArCl^+)$	Mass shift	AsO^+	1.0	In

Table 2 (continued). Acquisition parameters.

Element	Q1/Q2	Main interferences	Scan method	Measured ion	Integration time (s)	ISTD
Se	78/78	$ArAr^+$	On-mass	Se^+	3.0	In
Rb	85/85		On-mass	Rb^+	0.3	In
Sr	88/88		On-mass	Sr^+	0.5	In
Zr	90/106		Mass shift	ZrO^+	0.5	In
Nb	93/125	$CuNO^+$	Mass shift	$NbOO^+$	0.3	In
Mo	95/127	$CuOO^+$	Mass shift	$MoOO^+$	0.5	In
Ru	99/99	$ArCu^+$	On-mass	Ru^+	0.5	In
Rh	103/103	$ArCu^+$	On-mass	Rh^+	0.3	In
Pd	105/105	$ArCu^+$	On-mass	Pd^+	0.5	In
Ag	107/107		On-mass	Ag^+	0.3	In
Cd	111/111		On-mass	Cd^+	1.0	In
Sn	118/118		On-mass	Sn^+	0.5	In
Sb	121/121		On-mass	Sb^+	0.5	In
Te	125/125		On-mass	Te^+	3.0	In
Cs	133/133		On-mass	Cs^+	0.5	In
Ba	137/137		On-mass	Ba^+	0.5	In
Hf	178/194		Mass shift	HfO^+	0.5	In
Ta	181/213		Mass shift	$TaOO^+$	0.5	In
W	182/214		Mass shift	WOO^+	0.5	In
Re	185/185		On-mass	Re^+	0.5	In
Ir	193/193		On-mass	Ir^+	0.5	In
Pt	195/195		On-mass	Pt^+	0.5	In
Au	197/197		On-mass	Au^+	0.5	In
Tl	205/205		On-mass	Tl^+	0.3	In
Pb	208/208		On-mass	Pb^+	0.3	In
Bi	209/209		On-mass	Bi^+	0.3	In
Th	232/248		Mass shift	ThO^+	0.3	In
U	238/270		Mass shift	UOO^+	0.3	In

Results and Discussion

BECs and DLs in 5% HNO₃ blank

Background equivalent concentrations (BECs) in 5% HNO_3 were obtained from the calibration plots for each analyte. Calibration plots for three alkaline elements (Li, Na, and K) are shown in Figure 1. The BECs for the three elements were 0.1, 6.1, and 5.4 ppt, respectively, indicating very low background signals obtained using the m-lens. Calibration plots for Si, P, and S are also given in Figure 1. The BECs for these challenging elements were 231, 7.2, and 84 ppt, respectively. P and S have relatively high first ionization potentials (IPs) and so are poorly ionized under cool plasma conditions. Using hot plasma conditions in this work, these poorly ionized elements – together with others such as B, Zn, As, Cd, Ir, Pt, and Au – were all measured at low ppt levels.

The BECs and 3σ DLs for all 49 elements in the 5% HNO_3 blank are shown in Figure 2. The BECs for most elements were below 1 ng/L (ppt) in solution. This value is equivalent to <1 μg/kg (ppb) relative to the solid Cu, taking the 1000x dilution into account. This sensitivity indicates that the 8900 ICP-QQQ method is suitable for ultratrace analysis of these impurity elements in high-purity Cu. Low ppt BECs were also achieved for alkali elements, Li, Na, and K, under the hot plasma conditions used. BECs at the 10s to 100s ppt-level were achieved for the most challenging elements: S (84 ppt) and Si (231 ppt).
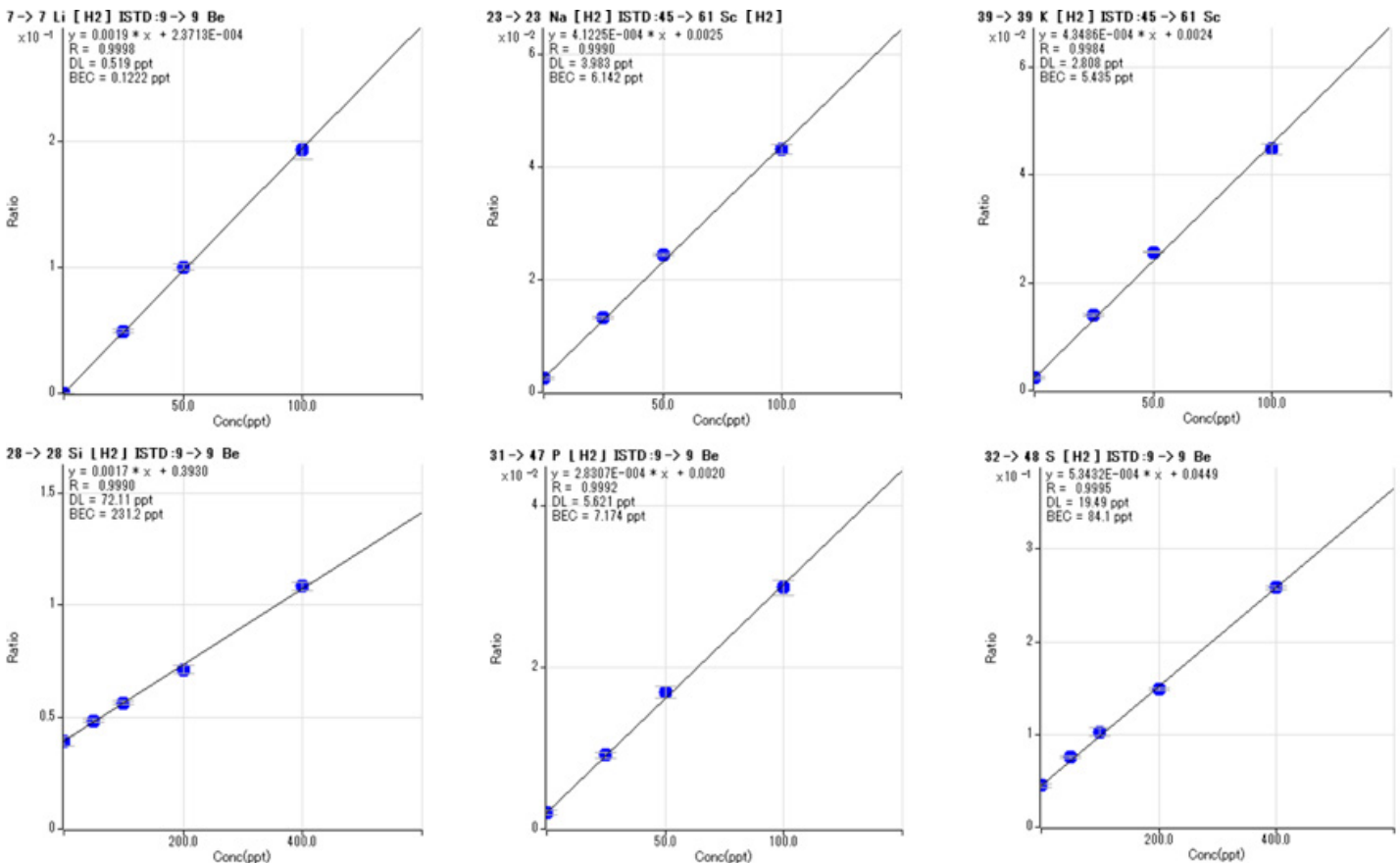

Figure 1. Calibrations for easily-ionized elements Li, Na, and K, and challenging elements Si, P, and S.
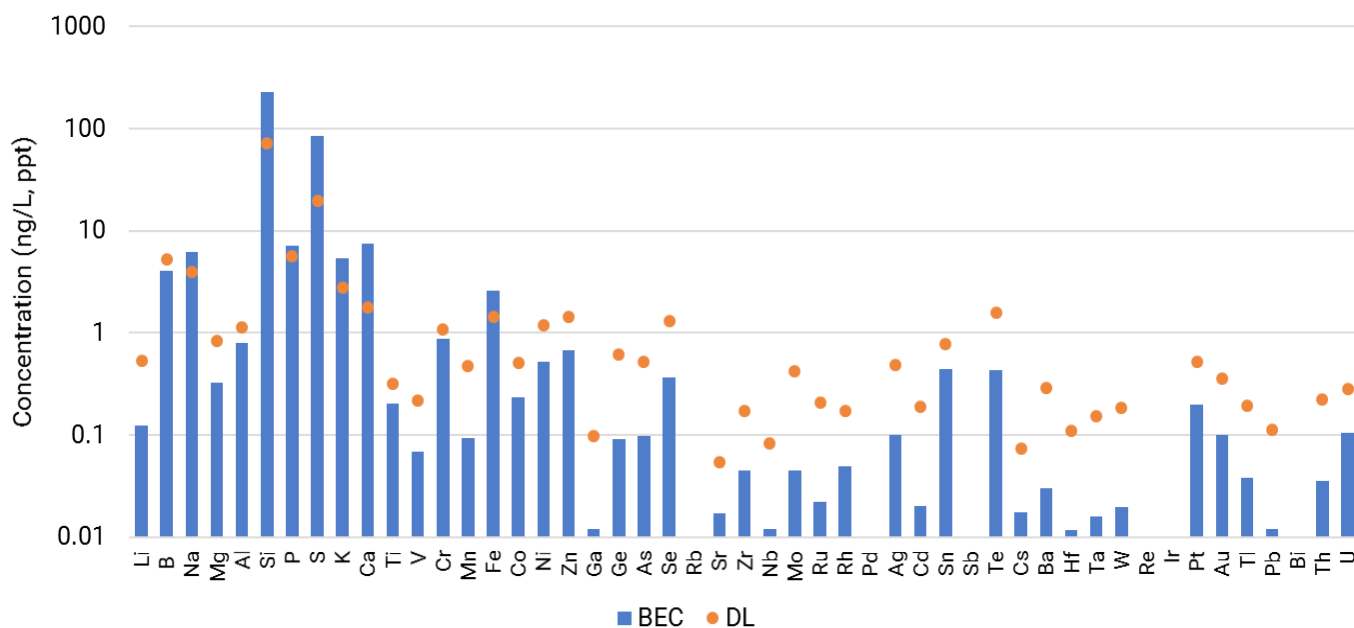
Figure 2. BECs and 3σ DLs for 49 elements in 5% HNO$_3$ blank. The BEC and DL for Rb, Pd, Sb, Re, Ir, and Bi could not be calculated, as the measured counts were zero in all replicates of the blank.

Determination of impurities in 0.1% 9N high purity copper

The 8900 ICP-QQQ method was used to determine the concentration of 49 elements in the 0.1% high purity copper solutions. ISTD correction was applied to correct for signal differences between the synthetic standards (with no Cu matrix) and the 0.1% Cu samples. Signal differences were all less than 30% between the non-matrix and Cu-matrix samples, demonstrating the robustness of the hot plasma conditions used.

All elements measured—apart from Si, S, and Te—were <10 ppt in the digest, as shown in Figure 3. Most elements were measured at 1 ppt or below, which is equivalent to <1 µg/kg (ppb) in the solid metal. The mixed O$_2$ + H$_2$ reaction cell gas removed the significant spectral interferences caused by ArCu$^+$ on Ru$^+$, Rh$^+$, and Pd$^+$ (see Table 2). Removing the interferences allowed the determination of these elements at single- or sub-ppt levels (equivalent to single- or sub-ppb in the solid metal).
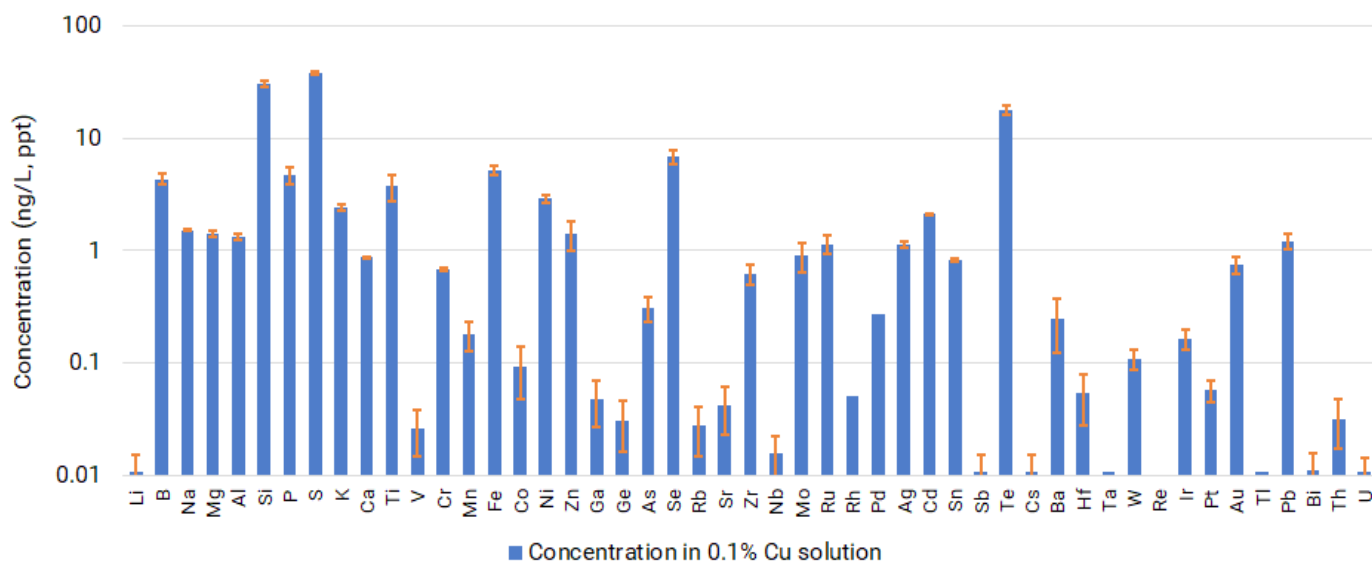

Figure 3. Measured concentrations of 49 elements in 0.1% 9N Cu sample (error bars = standard deviation for three samples). The values shown in ng/L (ppt) in solution) are equivalent to the values in µg/kg (ppb) in the original solid metal. The concentration reported for Re was 0.000 ppt. SDs were zero for Rh, Pd, Ta, Re, and Tl.
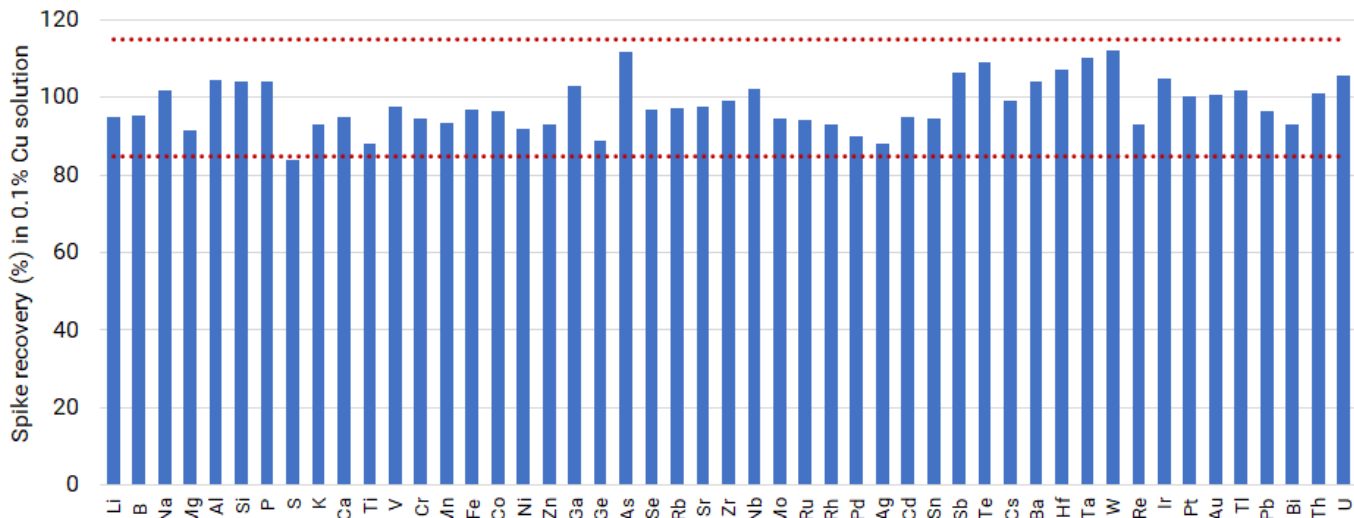
Spike recovery

Figure 4. Spike recovery test at 50 ppt (200 ppt for S, P, and Si) in 0.1% Cu solution. Most elements were within 90–110% recovery. The red lines indicate upper and lower limits of 85 to 115% recovery.

To validate the method, a spike recovery test was carried out for all 49 impurity elements. A 0.1% 9N copper blank solution was spiked at 50 ppt (200 ppt for Si, P, and S). The recoveries were within 84-112% for all 49 elements, with most being within 90-110%, as shown in Figure 4.

Conclusions

Ultratrace level impurities can be analyzed quickly and accurately in high purity copper metal digests using the Agilent 8900 ICP-QQQ. The optional m-lens ensures that the background signals for the alkali elements are minimized under hot plasma conditions. Using MS/MS mode with a mixed cell gas ($O_2 + H_2$), the method delivered the following performance benefits:

- Low ppt level BECs were achieved for most impurities, including the alkali elements, using matrix-tolerant hot plasma conditions.

- Low-level BECs at the 10s to 100s ppt-level were obtained for sulfur and silicon—the most challenging elements to measure using ICP-MS.

- No matrix matching for Cu matrix was required, as ISTDs corrected for matrix differences between the standards (in 5% HNO_3) and the samples (in 0.1% Cu).

- Using the fast and simple method with a single, mixed cell gas mode, a total of 49 elements were determined at ultralow levels in 0.1% high purity Cu sample.

References

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