Analysis of High Purity Cu Using High Sensitivity LA-ICP-Q-MS

K. Warnken[1], J. Jimenez[2], J.D. Wills[3], and L. Rottmann[3]

[1] Thermo Scientific, 4410 Lottsford Vista Rd., Lanham, MD 20706, USA

[2] Thermo Scientific, C/. Valportillo I, nº 22. Edificio Caoba, 28108. Alcobendas. Madrid, Spain

[3] Thermo Scientific, Hanna Kunath Str. 11, Bremen, 28199, Germany

Overview

Purpose: To illustrate the use of a new quadrupole ICP-MS system for the bulk determination of trace metals in >5N Copper.

Methods: Samples were analyzed for 11 analytes, including ^{56}Fe, ^{60}Ni, ^{68}Zn, ^{75}As, ^{78}Se, ^{107}Ag, ^{118}Sn, ^{121}Sb, ^{125}Te, ^{208}Pb and ^{209}Bi using laser ablation coupled to quadrupole ICP-MS in KED mode.

Results: Fully quantitative analysis of solid Cu by laser ablation ICP-MS was performed and demonstrates that contaminants can be detected at sub ppm levels.

Introduction

Of all the elements in the periodic table, Copper is mined and used on a global scale at a rate behind that of only Al and Fe. Copper is sought for its high electrical conductivity, which is second only to Ag, and is used in all types of wiring applications from buildings to cars and motors. Copper exists at different purity levels, e.g. the standard grade of 99.9 all the way up 99.999999 (known as 8-9's Cu), where the highest purity Cu is very limited in use because of the expense to purify it. The world's Cu miners require analytical techniques to determine the level of contaminants in their Cu and current methods include Arc/Spark OES and XRF. However, these techniques often do not meet the ppb(s) detection limit requirements currently being sought by the Cu producers.

Laser Ablation Inductively Coupled Plasma Mass Spectrometry (LA-ICP-MS) has become more appealing as a method for the analysis of pure Cu over other bulk techniques, which simply do not have the detection capability to match ICP-MS. The new Thermo Scientific iCAP Q ICP-MS, with its excellent sensitivity and background levels, is thus ideally suited for the measurement of metal contaminants in pure Cu. Quantitative analysis by Laser Ablation ICP-MS is largely dependent on the availability of calibration standards. While this has long been a serious area of contention for LA-ICP-MS, the availability of solid standards is making the technique more widespread with the eventual goal of meeting the demands of the production laboratory.

Methods

Sample Analysis

Samples were analyzed for 11 analytes, including ^{56}Fe, ^{60}Ni, ^{68}Zn ^{75}As, ^{78}Se, ^{107}Ag, ^{118}Sn, ^{121}Sb, ^{125}Te, ^{208}Pb and ^{209}Bi, utilizing the iCAP Q ICP-MS with the New-Wave Research NWR-213 laser ablation platform. Calibration was carried out using standards from CopperSpec, Inc., (www.copperspec.com) with the following concentrations: 0.1, 0.5, 3.0 and 5.0 ppm. The method was validated by measuring the European Reference Materials (ERM) EB383 and EB384. Each standard and reference standard was measured in duplicate using a 1 min scan line, after first pre-ablating the surface, on consecutive days.

ICP-MS instrument settings

The iCAP Q ICP-MS was operated in KED mode and instrument set-up was performed using the Autotune wizard on NIST 612 glass with a limit of ThO^+ of <0.3% (STD mode). The instrument was configured with a 2.0 mm quartz injector and a 2.8 mm skimmer cone insert. Newly developed flatapole based technology in the QCell (filled with100% He) was used for interference removal.

TABLE1. iCAP Q instrument parameters used for the analysis of solid Cu.

Parameter	Value
Forward Power (W)	1550
Pole Bias (V)	-18.0
CCT Bias (V)	-22.0
Sampling Depth (mm)	5.0
Nebulizer Flow (mL min^{-1})	790
(Laser cell) He Flow (mL min^{-1})	800
(QCell) He Flow Rate (mL min^{-1})	5.20
Injector Type; Size	Quartz; 2.0mm ID

Laser Ablation instrument settings

The NWR213 is a frequency quintupled 213 Nd:YAG laser, which is capable of an energy of ~3.5 mJ pulse^{-1}. The sample chamber is a two volume large format cell, with a sampling size of 100mm x 100mm. Helium was introduced into the laser cell using the on-board mass flow controller at a rate of 800 mL min^{-1} and mixed with Argon just prior to the torch. A 60 sec scan line was positioned on each of the four standards and the two reference materials. Pre-ablation of the surface was carried out, due to severe contamination of Fe and Zn. After pre-ablation, two additional passes were made and the results averaged and compared to the certified values.

TABLE 2. Laser parameters used for the analysis of solid Cu using the NWR-213.

Parameter	Value
Wavelength (nm)	213
Energy (mJ)	3.7
Repetition Rate (Hz)	20
Spot Size (µm)	250 (Focused Beam)
Scan Rate (µm s^{-1})	15

FIGURE 1. Thermo Scientific iCAP Q ICP-MS

Results

The method detection limits were determined over 3 consecutive duplicate runs of the 0.1 ppm Cu standard (n=6; 1 min scans). The analytical figures of merit are given in Table 3. With the exception of Fe and Se, which showed detection limits of 0.1 and 0.46 ppm respectively, limits of detection were <100 ppb were achieved with the use of pure He. If lower detection limits for Se are required, pure H_2 could be used in place of pure He. Elements such as Sb, Pb and Bi showed single digit ppb detection limits.

TABLE 3. Analytical figures of merit for the analysis of pure Cu by laser ablation ICP-MS. The IDL is calculated as three times the standard deviation of two runs conducted on consecutive days.

Analyte	Mass (amu)	Dwell Time (sec)	Mode	Resolu-tion	Sensitivity (cps ppb^{-1})	R value	BEC (ppb)	IDL (ppb)
Fe	56	0.050	KED (He)	Normal	1.7	0.9983	170	100
Cu	65	0.050	KED (He)	High	-	-	-	-
Ni	60	0.050	KED (He)	Normal	1.1	0.9999	36	26
Zn	68	0.050	KED (He)	Normal	0.26	0.9983	74	43
As	75	0.050	KED (He)	Normal	0.22	0.9998	92	69
Se	78	0.050	KED (He)	Normal	0.014	0.9947	300	460
Ag	107	0.050	KED (He)	Normal	6.2	0.9999	0	13
Sn	118	0.050	KED (He)	Normal	1.8	0.9999	40	40
Sb	121	0.050	KED (He)	Normal	1.7	0.9998	0	6.0
Te	125	0.050	KED (He)	Normal	0.037	0.9992	23	78
Pb	208	0.050	KED (He)	Normal	24	0.9994	0	4.0
Bi	209	0.050	KED (He)	Normal	31	0.9998	0	7.0

The % recovery of Cu, used as the internal standard to track the ablation process, over the course of the run is shown in Figure 2. It should be noted that each standard and the two unknowns were run in triplicate, with the first "pass" acting as a pre-ablation of the Cu surface. This was required due to the large amount of surface contamination observed with the first pass. Example calibration curves are shown in Figure 3 for the elements As, Ag and Bi.

FIGURE 2. The percent recovery of Cu used as an internal standard.

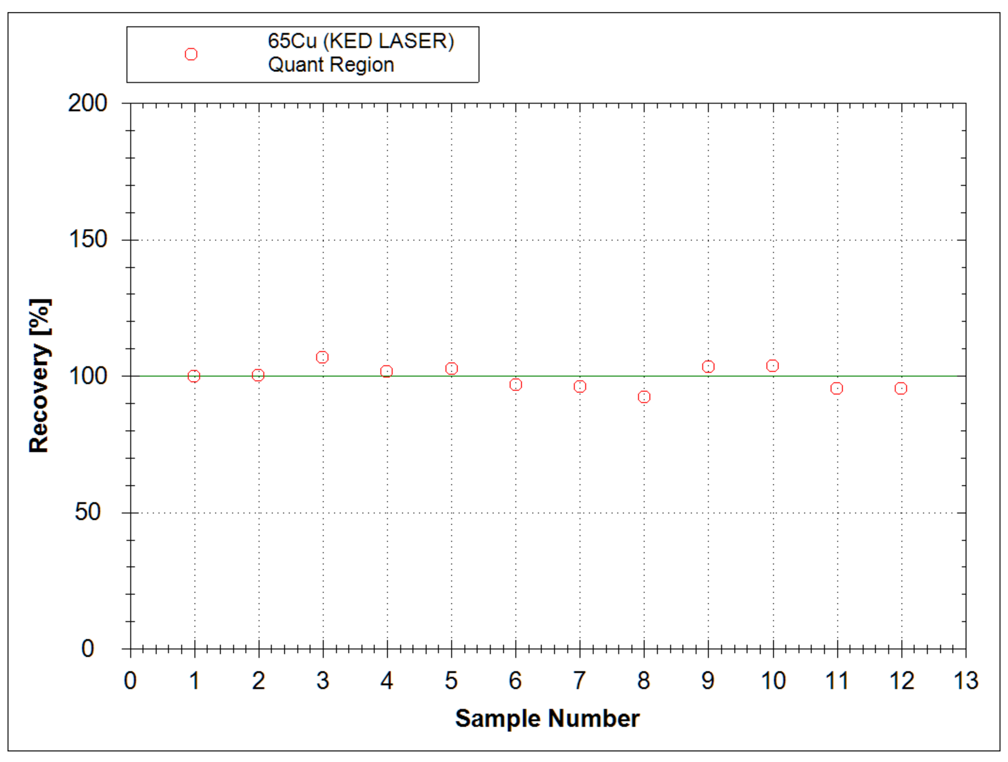
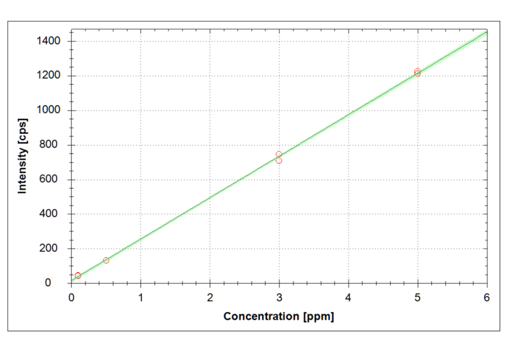
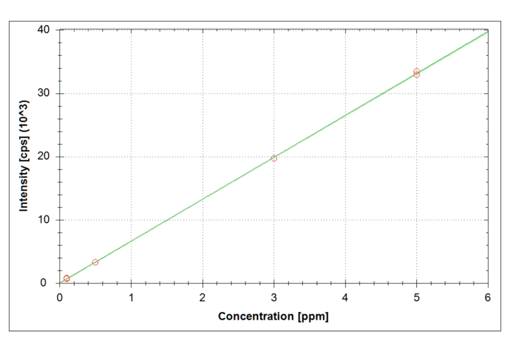


FIGURE 3. Calibration curves for the elements As, Ag and Bi

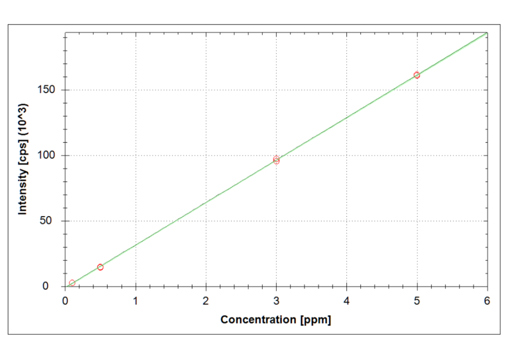
^{75}As



^{107}Ag



^{209}Bi



Time-resolved scans of Bi in the 0.1 ppm standard are shown both as individual plots and overlaid plots in Figure 4. Scan regions were set up to include a gas blank region from 0 to 20 seconds, followed by a quant region from 35 to 75 seconds, using the all new Thermo Scientific Qtegra software. The fully quantitative results, which were acquired in trQuant mode, for the reference standards BAM 383 and BAM 384 are given in Tables 4 and 5, respectively.

FIGURE 4. Time resolved scans of Bi in the 0.1 ppm calibration standard.

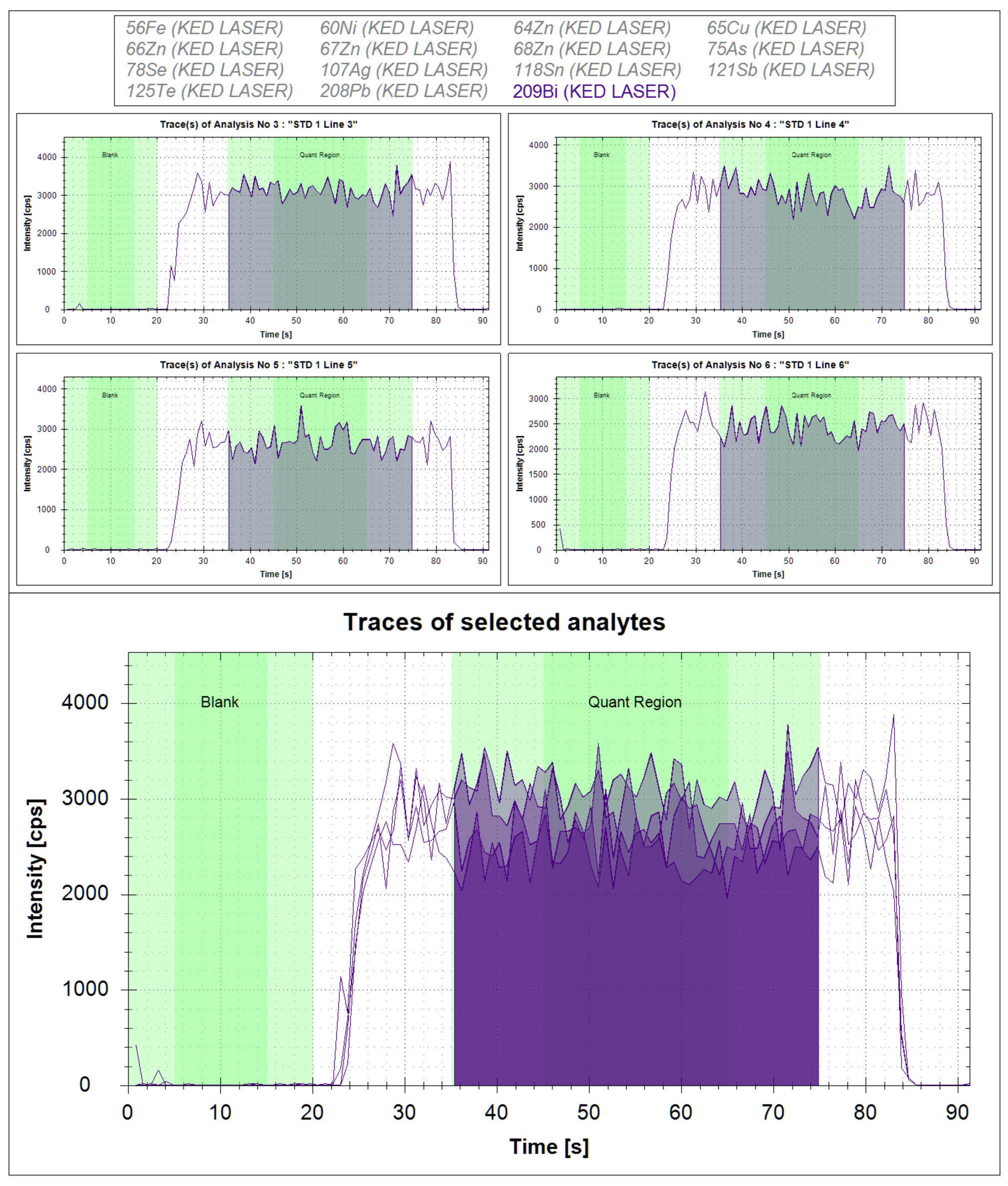


TABLE 4. Fully quantitative results for the standard reference material BAM 383 by Laser Ablation ICP-MS .

	^{56}Fe ppm	^{60}Ni ppm	^{68}Zn ppm	^{75}As ppm	^{78}Se ppm	^{107}Ag ppm	^{118}Sn ppm	^{121}Sb ppm	^{125}Te ppm	^{208}Pb ppm	^{209}Bi ppm
Cert. Value	10.9	3.59	7.80	1.93	1.16	4.70	4.70	1.44	1.40	1.31	1.02
Run 1	-	3.28	8.47	2.01	1.84	5.04	-	1.37	1.16	1.63	1.14
Run 1	10.9	3.23	8.14	1.96	1.12	5.04	5.00	1.36	1.22	1.64	1.14
MEAN	10.9	3.25	8.31	1.98	1.48	5.04	5.00	1.37	1.19	1.64	1.14
%RSD	-	1.0	2.8	1.7	34	0	-	0.52	3.9	0.43	0
%Rec.	100	91	106	103	127	107	106	95	85	125	112
Run 2	11.9	3.05	8.36	2.02	1.38	4.98	4.80	1.38	1.38	1.47	1.10
Run 2	13.3	2.99	8.25	2.07	1.51	4.99	4.81	1.35	1.01	1.48	1.10
Run 2	11.6	3.06	8.49	2.07	1.02	5.02	4.86	1.38	1.23	1.48	1.11
Run 2	11.6	3.07	8.41	2.08	1.37	5.02	5.00	1.42	1.12	1.51	1.12
MEAN	12.1	3.04	8.38	2.06	1.32	5.00	4.87	1.38	1.19	1.49	1.11
%RSD	6.7	1.1	1.2	1.2	16	0.45	1.9	1.9	13	1.2	0.93
%Rec.	111	85	107	107	114	106	104	96	85	114	109

TABLE 5. Fully quantitative results for the standard reference material BAM 384 by Laser Ablation ICP-MS .

	^{56}Fe ppm	^{60}Ni ppm	^{68}Zn ppm	^{75}As ppm	^{78}Se ppm	^{107}Ag ppm	^{118}Sn ppm	^{121}Sb ppm	^{125}Te ppm	^{208}Pb ppm	^{209}Bi ppm
Cert. Value	32.8	5.70	12.7	5.00	4.24	10.3	10.2	12.0	7.00	5.70	3.34
Run 1	30.3	5.64	15.4	5.22	4.01	10.5	9.46	12.4	6.18	6.36	3.61
Run 1	30.2	5.54	14.8	5.40	3.73	10.4	9.50	12.2	6.01	6.42	3.65
MEAN	30.2	5.59	15.1	5.31	3.87	10.4	9.5	12.3	6.10	6.39	3.63
%RSD	0.13	1.2	2.9	2.4	5.1	0.41	0.28	1.3	1.9	0.66	0.78
%Rec.	92	98	119	106	91	101	93	102	87	112	109
Run 2	33.2	5.14	15.8	5.71	3.39	11.0	9.95	13.1	6.67	6.46	3.62
Run 2	33.2	5.10	15.5	5.43	4.77	10.8	9.97	12.9	5.96	6.43	3.61
Run 2	34.2	5.01	16.0	5.52	4.94	10.8	9.90	12.7	6.76	6.41	3.61
Run 2	33.5	5.17	15.7	5.13	4.16	10.7	9.86	12.6	6.20	6.38	3.58
MEAN	33.5	5.11	15.8	5.45	4.31	10.8	9.9	12.8	6.40	6.42	3.60
%RSD	1.5	1.3	1.2	4.4	16	0.93	0.52	1.8	6.0	0.49	0.51
%Rec.	102	90	124	109	102	105	97	107	91	113	108

Conclusion

Here we have demonstrated fully quantitative analysis of solid Cu by laser ablation ICP-MS using commercially available calibration standards and standard reference materials. The high sensitivity of the iCAP Q ICP-MS in KED mode, with its proprietary Flatapole technology in pure He KED mode, makes possible the detection of low ppm levels of contaminants in solid Cu.