Elemental Scientific LASERS
INNOVATION TO ILLUMINATE

Applications Note

Purity Testing with LA-ICPMS

Analysis of Solid Copper

Introduction

Copper has become an ubiquitous component of the modern world as a result of its extensive use in electronic devices and wiring thanks to its high electrical conductivity. Consequently, copper is in high demand globally, and increasingly in its purest commercial form at 99.999999% purity for ultra-high specification components. The requirement to certify trace elements at such low levels is beyond the capabilities of XRF and Arc/Spark OES, hence more sensitive instrumentation is required to rapidly analyze contaminants at ppb levels without the need for extensive sample preparation/digestion. More sensitive alternatives such as GDMS/OES are significantly more expensive and are not suited to a high-throughput, industrial environment.

Laser Ablation Inductively-Coupled Plasma Mass Spectrometry (LA-ICPMS) meets these requirements. Advances in system and sample chamber technologies on the NWR (now ESL)-series laser ablation systems from Elemental Scientific enable the user to operate in a hands-off, autosampler-like mode while achieving detection limits in the parts per billion range. The improved availability of high-quality, certified reference materials has made LA-ICPMS a viable technique for the industrial determination of contaminants in copper.

Methods

A series of 4 calibration standards (0.1, 0.5, 3.0 and 5.0 ppm) from CopperSpec Inc. (www.copperspec.com) were placed in the sample chamber (2 Volume Cell) of a NWR213 laser ablation system connected to an iCAP™ Q ICPMS (Thermo Scientific). The method was validated by analysing the European Reference Materials (ERM) EB383 and EB384. Each standard and reference material was measured in duplicate using a 1 minute scan line, after first pre-ablating the surface. The analysis was repeated over consecutive days to determine experimental robustness (Table 1).

The NWR213 laser ablation system from Elemental Scientific is a 213 nm system suitable for use in a broad range of applications. The standard sample chamber is a two volume large format cell (100 mm x 100 mm) that can hold many samples at one time.

Helium was introduced into the laser cell using the standard on-board mass flow controller at a rate of 800 mL/min and mixed with Argon just prior to the torch. A 900 µm (60 second) 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. The ICPMS was operated in kinetic energy discrimination (KED) mode with He collision gas, and instrument setup was performed using the Autotune wizard on NIST 612 glass with a limit of ThO+ of < 0.3%. The instrument was configured with a 2.0 mm quartz injector and a 2.8 mm skimmer cone insert. Samples were analyzed for 11 isotopes: ^{56}Fe, ^{60}Ni, ^{68}Zn, ^{75}As, ^{78}Se, ^{107}Ag, ^{118}Sn, ^{121}Sb, ^{125}Te, ^{208}Pb and ^{209}Bi. ^{65}Cu was used as an internal standard (Table 2).

Table 1. Instrumental parameters for the analysis of solid Cu.

Parameter	Value
Forward Power	1550 W
Nebulizer Air Flow	790 mL/min
Ablation Cell He Flow	800 mL/min
Q-Cell He Flow	5.2 mL/min
Wavelength	213 nm
Fluence	7.5 J/cm^2
Repetition Rate	20 Hz
Spot Size	250 µm
Scan Rate	15 µm/s

Figure 1. NWR (now ESL) platform

Table 2. Analytical figures of merit for the analysis of pure Cu by laser ablation ICPMS. The IDL is calculated as three times the standard deviation of two runs conducted on consecutive days.

Analysis results of pure Cu								
Analyte	Mass (amu)	Dwell Time (s)	Mode	Resolution	Sensitivity (cps/ppb)	R^2 Value	BEC (ppb)	IDL (ppb)
Fe	56	0.05	KED (He)	Normal	1.7	0.9983	170	100
Cu	65	0.05	KED (He)	High	-	-	-	-
Ni	60	0.05	KED (He)	Normal	1.1	0.9999	36	26
Zn	68	0.05	KED (He)	Normal	0.26	0.9983	74	43
As	75	0.05	KED (He)	Normal	0.22	0.9998	92	69
Se	78	0.05	KED (He)	Normal	0.014	0.9947	300	460
Ag	107	0.05	KED (He)	Normal	6.2	0.9999	0	13
Sn	118	0.05	KED (He)	Normal	1.8	0.9999	40	40
Sb	121	0.05	KED (He)	Normal	1.7	0.9998	0	6
Te	125	0.05	KED (He)	Normal	0.037	0.9992	23	78
Pb	208	0.05	KED (He)	Normal	24	0.9994	0	4
Bi	209	0.05	KED (He)	Normal	31	0.9998	0	7

Results

The method detection limits were determined over 3 consecutive duplicate runs of the 0.1 ppm Cu standard (n=6; 1 minute scans). The analytical figures of merit are given in Table 2. 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. If lower detection limits for Se are required, pure H_2 could be used as a collision gas in place of He. Elements such as Sb, Pb and Bi showed single digit ppb detection limits.

Scan regions were set up to include a gas blank region from 0 to 20 seconds, followed by a quantitative region from 35 to 75 seconds, using the Thermo Scientific Qtegra™ software. Fully quantitative results for the reference standards EB383 and EB384 are given in Table 3.

Table 3. Fully quantitative results for the standard reference materials EB383 and EB384 by LA-ICPMS.

EB383 *(results in ppm)*

	^{56}Fe	^{60}Ni	^{68}Zn	^{75}AS	^{78}Se	^{107}Ag	^{118}Sn	^{121}Sb	^{125}Te	^{208}Pb	^{209}Bi
Cert. Value	10.9	3.59	7.8	1.93	1.16	4.7	4.7	1.44	1.4	1.31	1.02
Mean – Run 1	10.9	3.25	8.31	1.98	1.48	5.04	5	1.37	1.19	1.64	1.14
%RSD	< 0.1	1	2.8	1.7	34	< 0.1	< 0.1	0.52	3.9	0.43	< 0.1
%Rec.	100	91	106	103	127	107	106	95	85	125	112
Mean – Run 2	12.1	3.04	8.38	2.06	1.32	5	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

EB384 *(results in ppm)*

	^{56}Fe	^{60}Ni	^{68}Zn	^{75}AS	^{78}Se	^{107}Ag	^{118}Sn	^{121}Sb	^{125}Te	^{208}Pb	^{209}Bi
Cert. Value	32.8	5.7	12.7	5	4.24	10.3	10.2	12	7	5.7	3.34
Mean – Run 1	30.2	5.59	15.1	5.31	3.87	10.4	9.5	12.3	6.1	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
Mean – Run 2	33.5	5.11	15.8	5.45	4.31	10.8	9.9	12.8	6.4	6.42	3.6
%RSD	1.5	1.3	1.2	4.4	16	0.93	0.52	1.8	6	0.49	0.51
%Rec.	102	90	124	109	102	105	97	107	91	113	108

High-Throughput, Automated Analysis

The NWR266macro (now ESL266macro) laser ablation system is also available with optional sample automation for higher throughput and unattended analysis.

SelfSeal™ is a small-volume ablation chamber that creates a seal directly on the sample surface (Figure 2). Purging takes 5-7 seconds per sample, and the signal response is rapid with almost instant transport to the ICP and steady state signal (Figure 3).

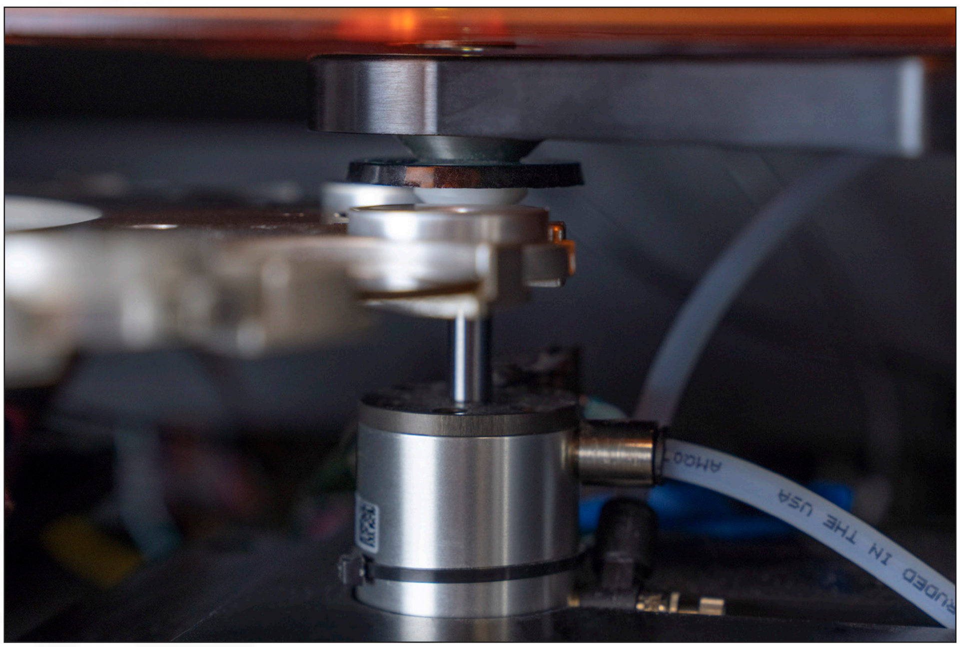

Figure 2. SelfSeal™ makes a seal on the sample surface.

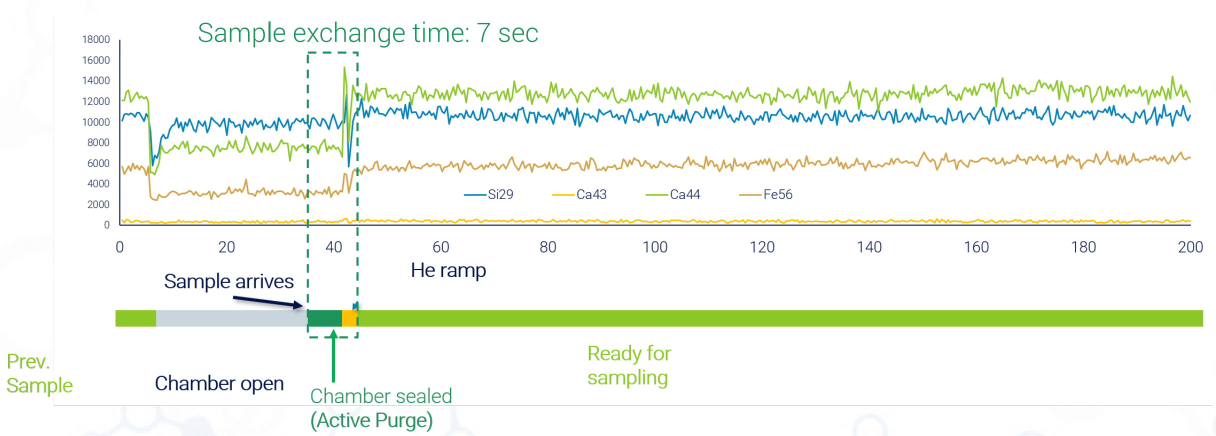

Figure 3. The purging/ramping time per sample is greatly reduced with NWRauto (now Laser SC).

SelfSeal™ can be augmented with the NWRauto carousel sample introduction system that holds 20 samples (Figure 4). Between ablations the carousel rotates to present a new sample to the SelfSeal™ chamber, reducing the “idle time” where the system is not measuring, to typically 16-20 seconds per sample. Carousel plates can be rapidly exchanged to further increase sample throughput. A standard sample chamber is greatly slowed by the sample exchange process of opening the chamber, loading samples, purging (120 seconds), locating samples, placing scans and running a batch, giving a typical idle time of 120-240 seconds per sample. NWRauto automates these processes, which has a profound improvement on throughput.

Figure 4. The carousel and SelfSeal™ on the NWRauto.

The carousel is suitable for a throughput of 20-100 samples per day. However, if the sample load exceeds this ESL can upgrade the NWRauto with full sample handling automation. Depending on analysis requirements it can handle up to 1000 samples per day. Figure 5 shows an NWRauto combined with a robot arm that delivers samples from the loading area to a barcode scanner and on to the carousel for analysis. ActiveView2 software driving the NWRauto creates a sample batch list that is pushed through to the ICP-OES or ICPMS automatically. After analysis the robot removes samples and deposits them back in the loading area or into a designated waste container. All the analyst needs to do is deliver samples to the instrument and start the sequence.

Figure 5. LaserTRAX with robot arm sample delivery and barcode scanner in a Class 1 laser safe enclosure.

Conclusions

Here we have demonstrated fully quantitative analysis of solid Cu by laser ablation ICPMS using commercially available calibration standards and standard reference materials. The high sensitivity of the iCAP™ Q ICPMS in KED mode makes possible the detection of low ppm levels of contaminants in solid Cu.

LA-ICPMS is an excellent analysis technique for major and trace bulk elemental determination of industrial samples with low ppm detection limits and precision < 3 %RSD achievable for many elements that outperforms spark source techniques, XRF and LIBS. LA-ICPMS can rapidly determine major and trace element concentration and, unlike glow discharge or spark source methods, can be readily applied to irregular sample geometry. Laser ablation can also perform spatial determination and depth profiling, for example, to identify inclusions, grain boundaries or defects. The analytical benefits of the LA-ICPMS technique make it an ideal choice for elemental analysis of industrial samples.

The ESL266macro can be augmented with options that offer a dramatic improvement in throughput and productivity. SelfSeal™, NWRauto and robotization reduce idle time of the system and reduce operator intervention while offering improvements in sensitivity.

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