Elemental Scientific LASERS
INNOVATION TO ILLUMINATE

Applications Note

Purity Testing with LA-ICP-MS

Analysis of Solid Copper

Current Situation

The current purity testing methods can produce unpredictable metal behavior and lack the detection capability to meet the stringent purity requirements for metals. The result can be unpredictable due to the noise of the spark source technique.

Customers use a solid sampling technique known as spark source to introduce samples into the ICP-OES. Applying an electric spark to understand the composition of ore is not sensitive or reproducible.

Some customers dissolve samples in hazardous and expensive acid. Dissolving samples is a time-consuming procedure and it might take multiple types of acid to determine elemental composition.

Solution

While reaching purity to match your customer's requirements, "When have you gone too far?" Laser ablation technology ensures accurate compositional information that customers are demanding. Macro analysis generates large ablations, which makes for highly sensitive analysis. The process eliminates the use of acid, therefore improving safety and reducing environmental impact. XRF and laser ablation can be used as complimentary techniques simultaneously determining major and trace element concentration. Quick analysis during the purity process is critical when determining purity levels. Laser ablation ensures constant analysis and a better understanding of the changes in elemental composition of metals.

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 these low levels is beyond the capabilities of techniques such as XRF and Arc/Spark OES, hence more sensitive instrumentation is required to analyze contaminants at ppb levels, preferably without the need for extensive sample preparation/digestion.

Laser Ablation Inductively-Coupled Plasma Mass Spectrometry (LA-ICP-MS) meets these requirements. Advances in system and sample chamber technologies on the NWR-series laser ablation systems from Elemental Scientific enable the user to operate in a hands-off, autosampler-like mode. The availability of high-quality, certified reference materials has increased, making LA-ICP-MS 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 ICP-MS (Thermo Scientific). 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 minute scan line, after first pre-ablating the surface, on consecutive days to determine experimental robustness (Table 1).

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

The NWR213 laser ablation system from Elemental Scientific is a 213nm system suitable for use in a broad range of applications. The standard sample chamber is a two volume large format cell (100mm x 100mm) 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 900µm (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 ICP-MS 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% (STD mode). The instrument was configured with a 2.0mm quartz injector and a 2.8mm 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 2. 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.

Analysis results of pure Cu								
Analyte	Mass (amu)	Dwell Time (s)	Mode	Resolution	Sensitivity (cps/ppb)	R^2Value	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	92%	Normal	1.7	0.9998	0	6
Te	125	0.05	103%	Normal	0.037	0.9992	23	78
Pb	208	0.05	92%	Normal	24	0.9994	0	4
Bi	209	0.05	103%	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 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.

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 Thermo Scientific Qtegra software. Fully quantitative results for the reference standards BAM 383 and BAM 384 are given in Table 3.

Table 3. Fully quantitative results for the standard reference materials BAM 383 and BAM 384 by LA-ICP-MS.

BAM 383 *(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	-	1	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
Mean – Run 1	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

BAM 384 *(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 1	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

Conclusions

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 makes possible the detection of low ppm levels of contaminants in solid Cu.

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