Analysis of Elemental Impurities in Electronic Grade Copper Sulfate using the Thermo Scientific iCAP 7400 ICP-OES Duo

James Hannan, Applications Chemist, Thermo Fisher Scientific, Cambridge, UK
Thomas Huang, Application Engineer, Joy Allied Technology inc, Taiwan
Vicki Wu, Application Manager, Joy Allied Technology inc, Taiwan

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Key Words
Electrical grade copper sulphate, $CuSO_4$, raw materials testing

Goal
This application note focuses on the analysis of electronic grade copper sulphate demonstrating the superior performance and high optical resolution of the Thermo Scientific™ iCAP™ 7400 ICP-OES Duo for the analysis of this complex matrix sample.

Introduction
As technology advances, increasingly sophisticated manufacturing techniques are required for electronic goods. The main electrical conductor of these technologies is high purity copper. Components such as High Density Interconnect (HDI) printed circuit boards, flip chips used in bumping connections and wafer components, are manufactured using high purity copper sulfate. Electroplating is used to bind the positive copper ions, from the copper sulfate, onto the required surface. As a result of this electroplating technique, any other positive ions present in the copper sulfate, such as iron, calcium or chromium, are also plated to the surface, producing impurities in the copper and reducing its conductive efficiency. Therefore any impurities in the copper sulfate must be quantified, prior to use, in order to maintain the high quality required.

Analysis of impurities in copper sulfate by Inductively Coupled Plasma-Optical Emission Spectrometry (ICP-OES) is an ideal choice of technique as it enables accurate, high throughput, multi-element analysis while requiring minimal sample preparation.

For this analysis the Thermo Scientific iCAP 7400 ICP-OES Duo was used as it provides most cost effective solution that has the required instrument parameter control and speed of analysis, while its axial plasma view provides the highest sensitivity required for trace analysis.

Sample and standard preparation
The solid electronic grade copper sulfate ($CuSO_4$) samples were dissolved in ultra pure deionzed (DI) water (resistivity >18 MΩ/cm). 5 g of solid sample was dissolved in 50 ml of DI water and made up to a final volume of 250 ml; these samples were then ready for analysis. Multi-element calibration standards were made at concentrations of 0, 20, 50 and 100 µg/L (ppb) and matrix matched to the samples (2% $CuSO_4$).

Method
A Labbook was created using the Thermo Scientific™ Qtegra™ Intelligent Scientific Data Solution to analyse the elements of interest, the elements and analytical wavelengths selected can be seen in table 1 and the measurement modes, acquisition parameters and sample introduction accessories used are shown in tables 2 and 3. Instrument calibration plots were created using the calibration standards created (0, 20, 50 and 100 µg/L).

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Table 1. Elements, analytical wavelengths used and detection limits (DL) achieved

Element	Wavelength (nm)	DL (ug/1)
Ag	328.068	1.0
As	189.042	2.3
Ca	393.366	0.04
Cd	226.502	0.15
Co	228.616	0.33
Cr	267.716	0.47
Fe	259.940	0.82
In	230.606	4.2
K	766.490	0.44

Element	Wavelength (nm)	DL (ug/1)
Mg	279.553	0.03
Mn	257.610	0.17
Na	589.592	0.20
Ni	231.604	0.39
Pb	168.215	4.1
Sn	189.989	0.67
Ti	336.121	0.16
Tl	190.856	2.2
Zn	206.200	0.23

Table 2. Measure modes and acquisition parameters

Parameter		Value
RF Power		1150 W
Plasma View		Axial
Nebulizer Gas Flow		0.45 L/min
Auxilary Gas		0.5 L/min
Integration time	Low	20 Seconds
	High	5 Seconds
Pump Rate		50 rpm
# Repeats		3

Table 3. Sample introduction accessories used

Accessory
K-type concentric glass nebulizer
Glass cyclonic spray chamber
2ml ID center tube

Results and discussion

The method detection limits for this method (MDL) were calculated by analyzing a matrix matched blank with ten repeats, then multiplying the standard deviation (SD) by a factor of 3. The calculated detection limits can be seen in table 1.

The suitability of the analytical method was demonstrated by analyzing a series of matrix spiked samples. 5 electronic grade copper sulfate samples were spiked with 50 µg/L of all the target elements. Both the spiked and unspiked samples were analyzed and their measured concentrations compared. The results of this analysis along with the spike recoveries (R) are shown in table 4. The spike recoveries of all elements, for all samples, are between 92% and 105%.

In order to demonstrate the method and instrument stability, a sample of electronic grade copper sulfate was spiked with all of the target elements at 50 µg/L and then analyzed repeatedly over a period of 60 minutes, the results of which can be seen in figure 1. The average results, standard deviation (SD) and relative standard deviation (RSD) can be seen in table 5. The relative standard deviations for all elements were less than 2%, with the exception of lead which was below 4%.

Table 4. Spiked and Unspiked sample concentrations and spike recoveries. ND – No determination (measured concentration below method detection limit)

Mg Element	Average (ppb)	SD (ppb)	RSD (%)
Ag	49.95	0.69	1.38
As	52.15	0.57	1.09
Ca	52.90	0.56	1.07
Cd	50.21	0.24	0.47
Co	53.35	0.34	0.63
Cr	51.71	0.49	0.94
Fe	62.50	0.55	0.88
In	53.47	1.02	1.90
K	48.16	0.86	1.79
Mg	51.76	0.47	0.91
Mn	50.94	0.43	0.84
Na	51.99	1.00	1.92
Ni	52.72	0.31	0.59
Pb	50.69	1.58	3.13
Sn	53.13	0.33	0.62
Ti	50.97	0.47	0.92
Tl	48.63	0.69	1.43
Zn	51.37	0.25	0.48

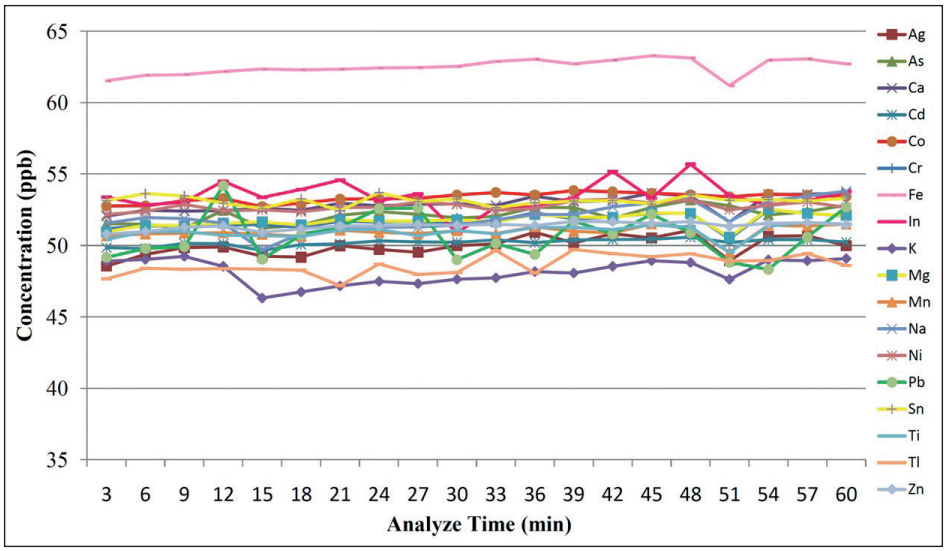

Figure 1. Stability test - $CuSO_4$ solution spiked

Table 5. Average, SD and RSD - $CuSO_4$ solution spiked

Element	Units	346 50X	348 50X	484 50X	486 50X	346 50X +50ppb	R (%)	348 50X +50ppb	R (%)	484 50X +50ppb	R (%)	486 50X +50ppb	R (%)
Ag	ppb	ND	ND	ND	ND	48.26	96.52	49.30	98.60	48.95	97.90	48.66	97.32
As	ppb	ND	ND	ND	ND	50.51	101.03	50.24	100.48	51.77	103.54	52.08	104.16
Ca	ppb	0.62	1.16	0.56	1.77	50.96	100.69	51.47	100.62	52.04	102.96	52.31	101.07
Cd	ppb	ND	ND	ND	ND	49.08	98.16	49.09	98.18	50.38	100.76	49.97	99.94
Co	ppb	ND	ND	ND	ND	50.31	100.62	50.38	100.76	51.73	103.46	51.20	102.40
Cr	ppb	0.49	ND	ND	0.46	49.56	98.14	49.55	99.10	50.65	101.30	50.94	100.96
Fe	ppb	8.38	9.38	7.35	12.63	57.57	98.38	58.01	97.25	57.58	100.47	62.57	99.88
In	ppb	ND	ND	ND	ND	47.21	94.42	47.70	95.40	48.19	96.38	48.32	96.64
K	ppb	ND	ND	ND	ND	49.19	94.38	46.24	92.48	47.33	94.66	46.70	93.40
Mg	ppb	0.18	0.25	0.20	0.36	49.73	99.09	49.43	98.37	50.57	100.74	50.35	99.98
Mn	ppb	ND	ND	ND	ND	49.00	98.00	48.88	97.76	49.91	99.82	49.74	99.48
Na	ppb	0.82	1.13	1.62	1.09	51.71	101.77	50.33	98.41	51.83	100.42	50.94	99.69
Ni	ppb	ND	ND	ND	ND	50.53	101.06	50.79	101.58	51.98	103.96	51.74	103.48
Pb	ppb	ND	ND	ND	ND	47.27	94.54	46.05	92.10	50.72	101.44	47.65	95.30
Sn	ppb	ND	ND	ND	ND	48.16	96.32	48.33	96.66	49.80	99.60	49.45	98.90
Ti	ppb	ND	ND	ND	ND	48.83	97.66	48.65	97.30	49.78	99.56	49.89	99.78
Tl	ppb	ND	ND	ND	ND	46.18	92.36	46.18	92.36	47.05	94.10	46.78	93.56
Zn	ppb	ND	ND	ND	ND	49.71	99.42	51.25	102.50	51.13	102.26	50.30	100.60

Conclusion

The low relative standard deviations derived from the stability study, combined with the % recovery values of the sample spikes, shows the high level of accuracy and precision of analytical results obtained with the iCAP 7400 ICP-OES Duo. The good method detection limits achieved also show that the iCAP 7400 ICP-OES Duo can easily perform the analysis of electronic grade copper sulfate required for electronic factories, semiconductor plants, precious metal technology sites and other electronic grade raw materials testing.

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Africa-Other +27 11 570 1840
Australia +61 3 9757 4300
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