

Analysis of Pure and Ultra-Pure Copper by Optical Emission

ARL 4460 Metals Analyzer

Key Words

- ARL 4460
- Pure and Ultra-Pure Copper
- Metals Analyzer
- Optical Emission

Introduction

Due to its high electrical and thermal conductivity, copper is the preferred and predominant metal used in the electrical industry. In order to obtain the required properties, unalloyed high purity copper is almost always used.

Composition is one of the most important criteria governing high electrical conductivity. Impurities such as Fe, As and P can significantly decrease the conductivity, modifying the mechanical properties of the copper and must be kept as low as possible. For OFHC (oxygen-free high conductivity) copper, 99,99% Cu, with limited S and P content is essential.



Our long experience in metals analysis comes from an installed base of over 10,000 spectrometers worldwide. The Thermo Scientific ARL 4460 is the answer to your

metallurgical analysis needs, whether they be incoming material control or metal QC and production analysis. Working 24 hours a day and 7 days a week, the ARL 4460 delivers dependable performance year after year.

The ARL 4460 Metals Analyzer can determine simultaneously up to 60 elements in one minute. Specific performance is detailed in this application summary.

Using the ARL 4460 Metals Analyzer, sample analysis time, sensitivity, precision, accuracy and maintenance operations have all been substantially improved in the analysis of pure and ultra-pure copper.

The high performance of the ARL 4460 will not only completely meet your analytical needs of today, but also those of tomorrow.

Pure and ultra-pure copper

Two main refining processes are used to produce pure and ultra pure copper:

- Pyrometallurgy
- Wetmetallurgy enrichment

Depending on the purity requested, a second pyrometallurgical procedure may also be applied.

- Different levels of purity are required for various applications
- High purity copper (electrolytic cathode copper) for electrical power transmission or electronic applications
- Fire-refined copper, mostly used to produce alloys like brass or bronze or Cupro-Nickel

Sampling copper cathodes

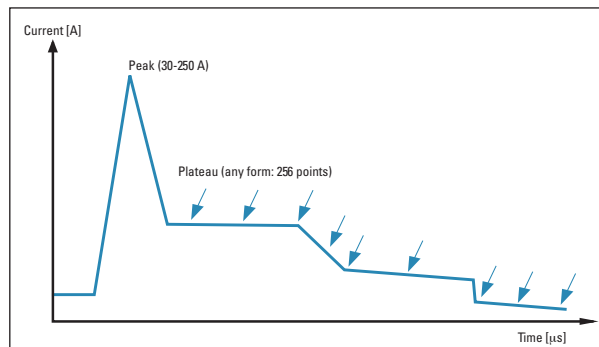
Sampling is a major concern for pure copper analysis, due to the difficulty in producing a representative copper cathode sample. Norms (i.e ASTM B115) outline optimum sampling method procedures.

Current Controlled Source (CCS)

The Thermo Scientific Current Controlled Source presents significant advantages in comparison to any other spark generator currently used for OES. It is the only servo-controlled “digital source” on the market.

The current waveform is computer controlled and can be selected for each type of metal. The high degree of flexibility in selection of peak current (250 A max.), frequency (1000 Hz max.) and current waveforms enables the optimization of all analytical figures.

The very compact design close to the spark stand, enclosed in a Faraday cage, suppresses RF leakage and improves general stability (less current lost in connecting cables).

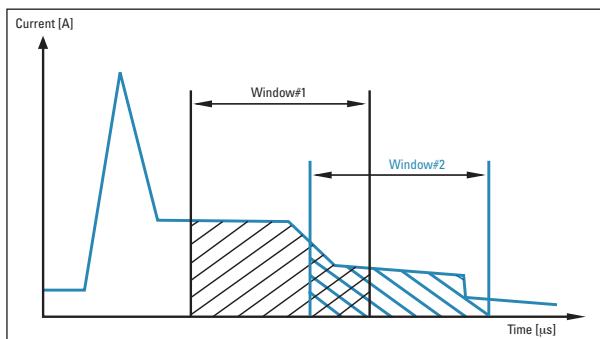


Time Resolved Spectroscopy (TRS)

For the duration of an individual spark, the line-to-background ratio varies significantly. The selection of the most appropriate period of the spark when data acquisition takes place, improves sensitivity and precision for trace analysis.

TRS removes the first peak of current (high background) and selects a "window" (the best section of the "plateau" current) for each element.

In the case of spectral line interferences, where there is a significant difference in the excitation potential of the analyte and of interfering lines, the accuracy of calibration can be substantially improved using TRS.



Sample preparation

A lathe or milling machine is used to prepare the surface of the sample, since grinding may contaminate the sample surface.

Sample analysis time

The analysis time taken between the start of the analysis and the display of the result is 19 s (also if O is analyzed).

Using the CCS source, the sample analysis time is reduced by 40 to 55 % when compared to conventional excitation methods.

Factory calibration (CARL)

Thermo Scientific optical emission spectrometers can be factory calibrated for pure and ultra-pure copper utilizing CARL, a very sophisticated multi-variable regression tool that corrects for matrix effects as well as spectral interferences. CARL can provide an immediate "turn-key" system which gives the user the highest accuracy possible. For each quality we use certified materials as standard samples and supplies setting-up samples with each instrument to maintain the accuracy of the calibration.

Our company provides calibrations for 2 qualities of copper:

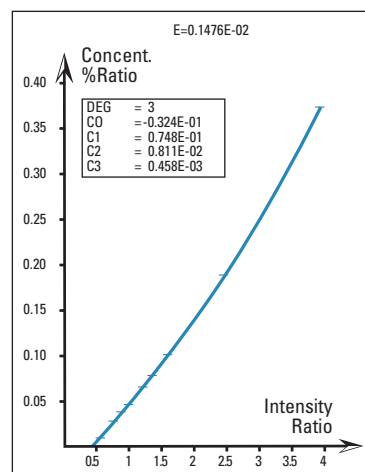
- Ultra-pure copper
- Pure copper

Accuracy

Accurate analysis can be attributed to a number of factors:

- The accuracy and quality of the calibration standards
- Precision
- Matrix matched calibration standards
- High energy pre-burn, to reduce or eliminate matrix effects
- Applying appropriate correction equations to reduce spectral interferences

The example shown below illustrates a calibration curve obtained for oxygen in pure copper.



The table below shows the analysis of the CRM 075 (International Certified Reference Material) and the comparison to the certified values.

EL.	CERTIFIED VALUE [PPM]	INTERLABO. 3 S [PPM]	MEASURED VALUE [PPM]	DIFFERENCE [PPM]
Ag	12.2	0.6	12.1	-0.1
As	3.74	0.3	3.7	-0.04
Bi	1.44	0.11	1.7	0.26
Cd	2.57	0.18	2.9	0.33
Co	2.5	0.18	2.4	-0.1
Cr	0.89	0.08	1.1	0.21
Fe	9	0.6	8.4	-0.6
Mn	3.23	0.3	3.1	-0.13
Ni	1.45	0.15	1.4	-0.05
O	14		18	4
Pb	3.27	0.15	3	-0.27
S	7		5.2	-1.8
Sb	2.56	0.23	2.9	0.34
Se	1.26	0.11	1.4	0.14
Sn	1.09	0.1	1.1	0.01
Te	1.52	0.08	1.3	-0.22
Zn	3.47	0.12	3.59	0.12

Table 1: ARL 4460 - Typical detection limits (3 sigma) and precision values (1 sigma) for PURE COPPER

ELEMENT	Ag	Al	As	Au	B	Be	Bi	Cd	Co	Cr	Fe	Mg	Mn
TYPICAL DL [PPM]	< 0.1	< 0.1	0.3	0.2	0.2	< 0.1	0.3	0.1	0.5	0.3	0.3	< 0.05	< 0.1
GUARANTEED DL [PPM]	0.2	0.2	0.5	0.5	0.4	0.2	0.6	0.3	1.0	0.6	0.6	0.1	0.1
Level [ppm]	SD	SD	SD	SD	SD	SD	SD	SD	SD	SD	SD	SD	SD
1	< 0.1	0.15	0.15	< 0.1	0.15	< 0.1	0.15	0.1				0.05	< 0.1
5	< 0.1	0.2	0.2	< 0.1	0.2	0.1	0.2	0.15	0.5	0.1	0.2	0.1	< 0.1
10	0.10	0.2	0.3	0.1	0.3	0.2	0.3	0.25	0.5	0.1	0.2	0.1	0.1
20	0.2	0.3	0.4	0.15	0.5	0.4	0.5	0.4	0.6	0.15	0.3	0.15	0.1
50	0.35	0.5	0.8	0.3		0.7	1.0	1.0	1.0	0.25	0.5	0.3	0.2
100	0.7	0.8	1.5			1	2.0	1.7	1.7	0.5	1.0	0.5	0.4
200	1.3	1.5	3.0			1.6	4.0	3.5	3.0	1.0	1.7	1.0	0.7

ELEMENT	Ni	O	P	Pb	S	Sb	Se	Si	Sn	Te	Ti	Zn	Zr
TYPICAL DL [PPM]	0.2	8	0.2	0.6	0.15	1.0	0.2	0.2	0.3	1.0	0.1	1.0	0.1
GUARANTEED DL [PPM]	0.4	15	0.4	1.3	0.3	2.0	0.4	0.3	0.5	1.8	0.15	1.5	0.3
Level [ppm]	SD		SD	SD	SD	SD	SD	SD	SD	SD	SD	SD	SD
1	0.15		0.3		0.1		0.1	0.1			< 0.1		0.1
5	0.2		0.3	0.4	0.2	0.3	0.2	0.1	0.25	0.8	0.12	0.4	0.2
10	0.25		0.4	0.5	0.3	0.4	0.25	0.15	0.35	0.9	0.2	0.5	0.3
20	0.3		0.6	0.6	0.5	0.5	0.5	0.2	0.5	1.0	0.4	0.6	0.5
50	0.6	3.5	1.0	1.2	1.2	1.0	1.0	0.5	1.0	1.5	0.9	1.0	1.2
100	1.0	5	1.5	2.0	2.5	2.0	2.0	0.7	2.0	2.5	1.7	1.7	2.5
200	2.0	8	3.0	4.0	5.0	3.5	4.0	1.3	4.0	4.0	3.5	3.0	4.0
1000		27											

Table 2: ARL 4460 - Typical detection limits (3 sigma) and precision values (1 sigma) for ULTRA-PURE COPPER

ELEMENT	Ag	Al	As	Au	B	Be	Bi	Cd	Co	Cr	Fe	Mg	Mn	Ni	O
TYPICAL DL [PPM]	0.05	0.08	0.1	0.12	0.05	< 0.01	0.25	0.1	0.1	0.05	0.2	0.02	0.04	0.15	6.5
GUARANTEED DL [PPM]	0.15	0.15	0.2	0.25	0.1	0.1	0.5	0.15	0.2	0.15	0.4	0.05	0.07	0.3	10
Level [ppm]	SD	SD	SD	SD	SD	SD	SD	SD	SD	SD	SD	SD	SD	SD	SD
0.5		0.025	0.025		0.015	0.005		0.02		0.015		0.007	0.01		
1	0.045	0.03	0.03	0.045	0.03	0.007	0.07	0.02	0.05	0.02	0.05	0.01	0.015	0.065	
2	0.05	0.04	0.04	0.05	0.06	0.015	0.08	0.03	0.05	0.02	0.05	0.02	0.015	0.07	
5	0.06	0.075	0.06	0.075	0.15	0.03	0.1	0.07	0.07	0.03	0.07	0.05	0.03	0.09	
10	0.08	0.15	0.09	0.1	0.25	0.06	0.2	0.15	0.1	0.05	0.08	0.1	0.04	0.1	
20	0.1	0.25	0.15	0.25	0.5	0.15	0.3	0.25	0.15	0.08	0.1	0.2	0.08	0.15	2
50	0.25	0.6	0.35	0.45	1	0.3	0.75	0.6	0.3	0.2	0.2	0.5	0.2	0.25	3
100	0.5	1	0.7	0.8	2.5	0.7	1.5	1.5	0.6	0.4	0.4	1	0.4	0.4	4
200	1.5	2.5	1.5	1.5	5	1.5	4.5	2.5	1	1	0.75	2	0.95	0.75	7

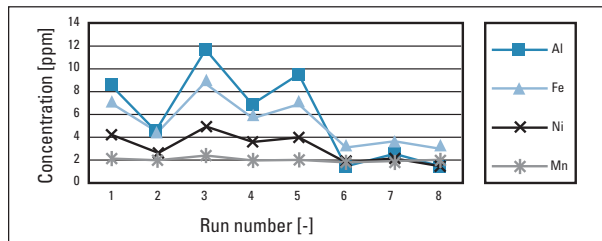
ELEMENT	P	Pb	Pd	Pt	Rh	S	Sb	Se	Si	Sn	Te	Ti	Zn	Zr
TYPICAL DL [PPM]	0.12	0.4	0.06	0.6	0.3	0.1	0.6	0.2	0.15	0.25	0.5	0.1	0.1	0.1
GUARANTEED DL [PPM]	0.25	0.7	0.25	2	0.5	0.2	1.8	0.4	0.3	0.4	1.0	0.15	0.2	0.25
Level [ppm]	SD	SD	SD	SD	SD	SD	SD	SD	SD	SD	SD	SD	SD	SD
0.5			0.015									0.01		0.02
1	0.04	0.085	0.02			0.035		0.06	0.05	0.07		0.015	0.05	0.03
2	0.045	0.1	0.025		0.1	0.05	0.25	0.08	0.06	0.08		0.03	0.06	0.045
5	0.07	0.15	0.045	0.45	0.2	0.1	0.3	0.15	0.07	0.1	0.3	0.06	0.08	0.1
10	0.1	0.2	0.07	0.45	0.35	0.2	0.4	0.2	0.09	0.2	0.4	0.1	0.1	0.2
20	0.2	0.35	0.15	0.5	0.5	0.35	0.55	0.4	0.15	0.3	0.5	0.25	0.15	0.35
50	0.4	0.75	0.3	0.6	1.5	0.8	1	0.9	0.25	0.7	0.9	0.6	0.3	0.9
100	0.85	1.5	0.6	0.9	2.5	1.5	2	1.5	0.5	1.5	1.5	1.5	0.6	2
200	2	3	1	1.5	4	3	3.5	3.5	1	2.5	3.5	3	1	4

Remarks: This data applies when homogeneous samples are prepared by recommended sample preparation methods. The precision given is typical performance. Guaranteed values will be 1.5 times higher. For multibase instruments, some analytical performance may vary based on the analytical line selected. Guaranteed DLs are calculated at 95 % confidence limit.

Memory effects

For testing purposes, a copper alloy (Al 8.7 %, Fe 6.5 %, Ni 0.73 %, Mn 0.35 %) was analyzed just before a pure Cu sample. The levels of pure Cu are obtained after 6 runs.

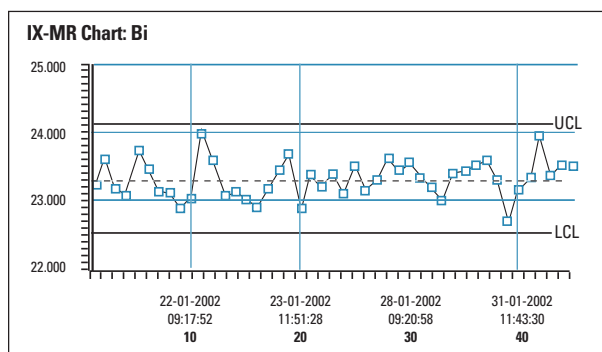
Therefore when the instrument is also used for the analysis of alloys, we recommend the utilization of different tables, electrodes and cups to avoid memory effects.



Stability

Stability of the instrument is of the utmost importance when performing routine analysis. Mid-term stability measured over 24 hours shows that the standard deviation achieved is below two times the precision value, which is excellent.

The example below shows the long-term stability of element Bi in ultra-pure copper recorded over a period of 10 working days without any intermediate drift correction. The standard deviation achieved remains in the range of the precision value, which is also excellent.



Performance guarantee

Our company guarantees the precision shown in Tables 1 and 2 using homogeneous samples and recommended sample preparation methods. The list will be updated as improvements are announced. Please contact your nearest Thermo Fisher Scientific office for the most recent values.

The precision is calculated from the formula:

$$SD(1\sigma) = \pm \sqrt{\frac{\sum_{i=1}^n (X_i - \bar{X})^2}{n-1}}$$

where:

- X_i the individual readings
- \bar{X} the arithmetic mean of the individual readings
- n the number of determinations

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The DL (Detection Limit) is defined as three times the standard deviation of the background expressed in concentration units.

Conclusion

The ARL 4460 provides not only state of the art technology, but also has all the total system features which meet the critical needs of the metals analysis markets.

- Unmatched hardware for stability and reliability
- Exceptional performance in detection limits, precision, accuracy, stability and memory effects, all this in minimum analysis time
- Most advanced software technology with HTML/Internet simple to use tools
- Potential to cover your future analytical needs
- Easy operation by unskilled worker or research chemist
- Widest range of metals analysis
- Adaptable to the automatic Sample Manipulation System: ARL SMS-2000
- Advanced technical/service support
- Laboratory accreditation guidance
- Immediate access to parts inventory

All these features allow you to optimize your productivity and to achieve the shortest payback times:

- Your investment costs are reduced thanks to the exceptional and widely recognized instrument lifetime and to the continuous upgrade possibilities (software and hardware)
- Your investment costs are reduced with the capability of the instrument to cover your future needs
- Your production costs are reduced by the fact that more accurate and reproducible analyses are available faster
- Your production costs are reduced by the increased instrument availability thanks to its high stability and drift corrections being less frequently required
- Your operating and maintenance costs are reduced through low consumption of drift correction samples, and through simple maintenance
- Your overall cost management is reduced by optimum utilization of materials and extremely low running costs compared to other methods

With over 70 years of experience and history of innovative technology, our company has become the world leader in OES metals analysis. We work with our customers to improve the efficiency of their analytical tasks and thereby increase productivity.

To see our complete OES product portfolio, visit www.thermoscientific.com/oes.

In addition to these offices, Thermo Fisher Scientific maintains a network of representative organizations throughout the world.

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