

Challenge

The precise determination of trace elements in the presence of line-rich matrix elements.

Solution

High-resolution ICP-OES with its high sensitivity and Dual View PLUS option provides an extended linear dynamic range from sub-ppb level to percentage range.

Determination of Precious Metals and Other Trace Elements in Copper and Copper Ore

Introduction

In the past years, the demand for precious metals has increased with the significant growth of the economy. Chalcopyrite (CuFeS_2) is the world's most important copper ore. During the extraction of copper, the ore is concentrated using flotation and smelting processes. Resulting waste matter, named slag, is separated and often contains high amounts of precious metals. Thus, copper ore, slags, and copper concentrates are analyzed for being a potential source of these valuable elements.

Due to its high sensitivity, robustness, and multi-element capabilities inductively coupled plasma optical emission spectrometry (ICP-OES) has become one of the most popular tools for the analysis of trace elements in various matrices, such as metal and metal ore samples. However, despite the unique features of ICP-OES, the determination of precious metals is drastically hampered by the emission spectra of matrix components. Especially ICP-OES instruments with relatively low resolution ($\Delta\lambda = 10\text{--}20\text{ pm}$) are prone to spectral interferences induced by line-rich matrices resulting in laborious calibration strategies or switching to alternative emission lines with less sensitivity. Copper ores

and intermediate products often contain (besides copper) high amounts of iron, cobalt, and other transition metals. It is known that iron is an extremely line-rich element emitting over 9,300 ICP spectral lines in a range from 200 to 400 nm, while copper possesses more than 1,400 lines. Unfortunately, these lines often overlap with the most prominent and sensitive emission lines of precious metals. Here we present the application advantages for trace element determination in copper and copper ore materials originating from the PlasmaQuant 9100 Elite. The optical system of the ICP-OES analyzer provides high resolution ($2\text{ pm @ }200\text{ nm}$) and output sections for the UV and visible wavelengths range (from 160 to 900 nm) with no spectral gaps. With access to more than 40,000 emission lines, the system offers to select alternative and interference-free lines with sufficient sensitivity for all investigated elements. Additionally, application advantages originating from the implementation of powerful software tools (ABC, CSI) for background correction and removing spectral interferences are presented.

Materials and Methods

Sample preparation

All laboratory equipment was washed with deionized (DI) water from a PURELAB system (18.2 MΩ-cm, ELGA LabWater, High Wycombe, England). Chemicals were of analytical reagent grade. All multi-element stock solutions were made up using single element and multi-element standard solutions (Merck, Sigma-Aldrich). The working standards were matrix-matched and prepared by serial volume/volume dilution in polypropylene tubes of the stock solutions using an acidic mixture of 5% (v/v) HNO₃ and 15% (v/v) HCl.

The samples ranged from different ores (copper ore, cobalt copper ore) to intermediates (e.g., black copper, copper concentrate, blister copper) of the refining process to the actual product, the so-called cathode copper. Approximately 0.5 g of each sample were accurately weighed (± 0.0001 mg) into a digestion vessel (DAP60). Afterwards, 2 (± 0.1) mL HNO₃ and 7.5 (± 0.1) mL HCl were added. The mixture was swirled carefully and left standing for at least 15 minutes before the vessel was closed. Subsequent heating

was performed stepwise (175 °C for 5 min, 190 °C for 5 min; 200 °C for 20 min) in a speedwave XPERT microwave digestion system. Afterwards the vessels were allowed to cool to room temperature to avoid foaming and splashing. The solutions were transferred to a graduated polypropylene tube, diluted to 50 mL with DI water, and centrifuged (1,125 g, 10 min). The supernatants were directly submitted to the analysis.

Calibration

Calibration levels for each element were chosen based on the expected concentration ranges. At least four calibration standards were used for each element, as described in Table 1. Selected calibration curves are shown in Figure 1. Nickel was measured in axial and radial view resulting in improved precision for trace and minor concentrations of the element in the same method.

Table 1: Concentration of calibration standards

Element	Unit	Cal. 0	Std. 1	Std. 2	Std. 3	Std. 4	Std. 5	Std. 6	Std. 7	Std. 8
Ag, Ni _{axial}	mg/L	0	0.05	0.1	0.2	0.5	1.0	-	-	-
Au, Ge, In, Ir, Pd, Pt, Ru, Rh	mg/L	0	0.05	0.1	0.2	0.5	-	-	-	-
Ni _{radial}	mg/L	0	-	-	-	-	1.0	5.0	10	20

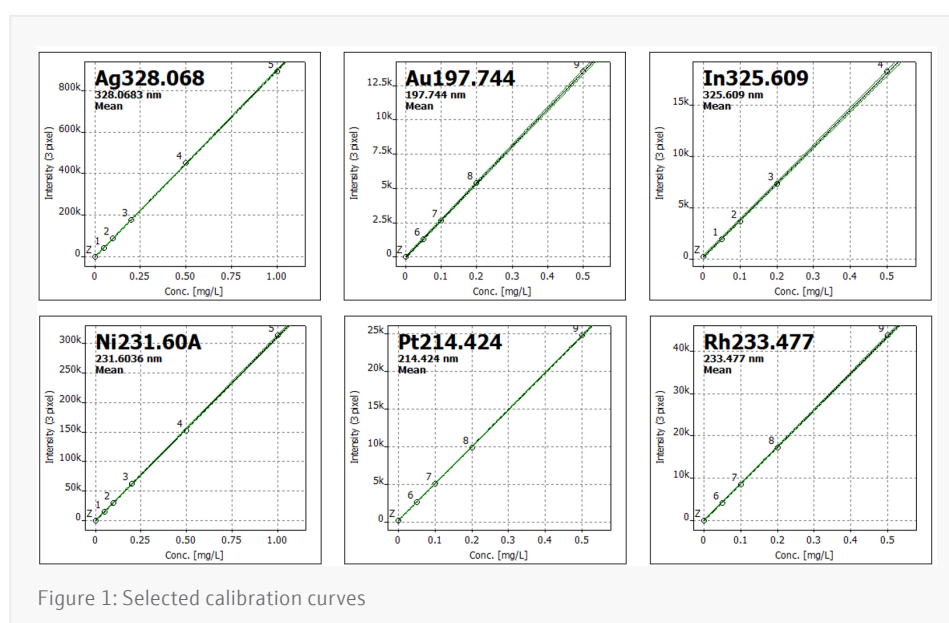


Figure 1: Selected calibration curves

Instrument settings

The analysis was performed on a PlasmaQuant 9100 Elite ICP-OES. The sample introduction components as well as the instrumental settings were selected to achieve a high level of sensitivity for trace elements in high matrix samples. In conjunction with this instrument, a Teledyne CETAC ASX-560 autosampler was used. Argon was used as the internal standard. A summary of individual settings and components is given in Table 2.

Table 2: Instrument settings

Parameter	Specification
Plasma power	1,350 W
Plasma gas flow	14 L/min
Auxiliary gas flow	0.5 L/min
Nebulizer gas flow	0.6 L/min
Nebulizer	Concentric, SeaSpray™, 2.0 mL/min, borosilicate
Spray chamber	Cyclonic spray chamber with dip tube, 50 mL, borosilicate
Outer tube/Inner tube	Quartz/Quartz
Injector	Quartz, ID: 2 mm
Sample tubing	PVC (black/black)
Pump rate	1.00 mL/min
Fast pump	4.00 mL/min
Measuring delay/Rinse time	55 s/25 s
Torch position	0 mm

Method and evaluation parameters

Table 3: Method parameters

Element	Line [nm]	Plasma view	Integration	Read time [s]	Evaluation		
					Pixel	Baseline fit	Correction
Ar	420,068	axial/radial	Peak	1	3	ABC ¹	-
Ag	328,068	axial	Peak	1	3	ABC	Ar ²
Au	197,744	axial	Peak	3	3	ABC	Ar
Ge	265,117	axial	Peak	3	3	static	Ar
In	325,609	axial	Peak	3	1	ABC	Ar
Ir	215,268	axial	Peak	3	3	static	Ar
Ni	231,648	axial	Peak	1	3	ABC	Ar
Ni	231,648	radial	Peak	1	3	ABC	Ar
Pd	360,995	axial	Peak	3	3	ABC	Ar
Pt	214,424	axial	Peak	3	3	static	Ar
Rh	233,477	axial	Peak	3	3	static	Ar
Ru	245,657	axial	Peak	3	1	ABC	Ar

1 ... Automated Baseline Correction

2 ... Argon line at 420,068 nm was used for internal standardization

Results and Discussion

It is well known that emission lines of copper and other transition metals (e.g., Fe, Ni, Co) interfere with the analytical lines of certain elements. Especially, the determination of precious metals and PGMs (platinum group metals) is hampered in such matrices. Usually, matrix matching is recommended for the calibration to overcome these issues. For this purpose, pure standards or reference materials are needed that show minimum contamination for the elements to be determined. One possibility to overcome the application issues is to use high resolution instruments which possess the capability of separating spectral interferences from the desired analytical line. The here presented results clearly demonstrate the enormous application advantages originating from the high resolution (2 pm @ 200 nm) of the PlasmaQuant 9100 Elite system in comparison to instruments with lower resolution allowing for choosing appropriate and sensitive analysis lines for most of the elements. The plasma geometry and the efficient removal of the plasma tail using argon (recycled from optical system purge) as counter gas leads to the high sensitivity of the instrument. This results in method-specific detection limits well below 1 mg/kg for all analytes.

Table 4: Results of the samples, instrumental (ILD) and method-specific limits of detection (MLD, considering dilution factor)

Element	ILD ¹ [µg/L]	MLD ² [mg/kg]	Copper ore [mg/kg]	Cobalt copper ore [mg/kg]	Black copper [mg/kg]	Copper concentrate [mg/kg]	Blister copper [mg/kg]	Cathode copper [mg/kg]
Ag	0.21	0.052	< MLD	< MLD	10.8	6.96	8.03	0.139
Au	1.68	0.422	< MLQ	1.67	< MLQ	3.78	0.535	< MLD
Ge	1.65	0.466	< MLD	< MLD	3.14	< MLD	3.72	< MLD
In	4.08	0.559	< MLD	< MLD	< MLD	< MLD	3.15	< MLD
Ir	4.35	0.538	< MLD	< MLD	< MLD	< MLD	< MLD	< MLD
Ni	0.37/2.77 ³	0.098/0.290 ³	92.7	1,636 ³	1,066 ³	49.6	394 ³	0.277
Pd	1.58	0.155	< MLD	< MLD	< MLD	< MLD	< MLD	< MLD
Pt	2.58	0.336	< MLD	< MLD	< MLD	< MLD	< MLD	< MLD
Rh	2.23	0.186	< MLD	< MLD	< MLD	< MLD	< MLD	< MLD
Ru	0.67	0.068	< MLD	< MLD	< MLD	< MLD	< MLD	< MLD

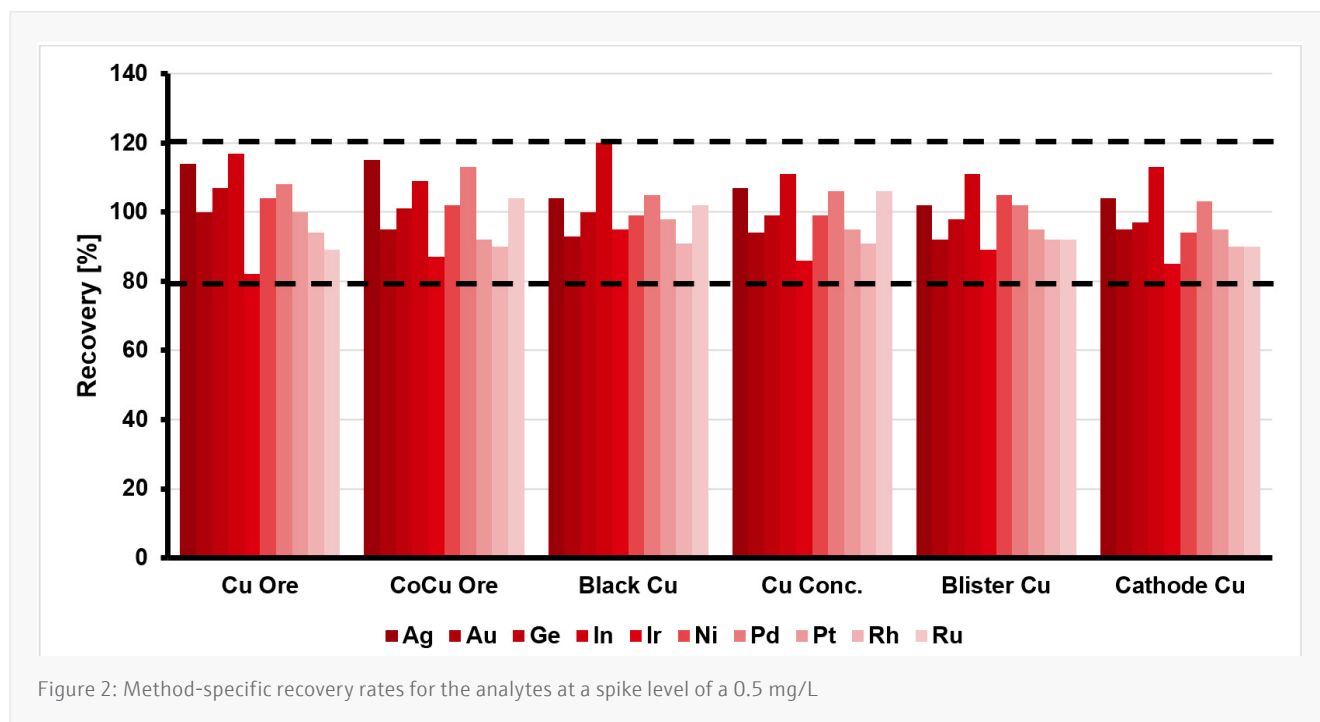
1 ... determined in ~5%/15% (v/v) HNO₃/HCl

2 ... determined in ~5%/15% (v/v) HNO₃/HCl + 10 g/L Cu

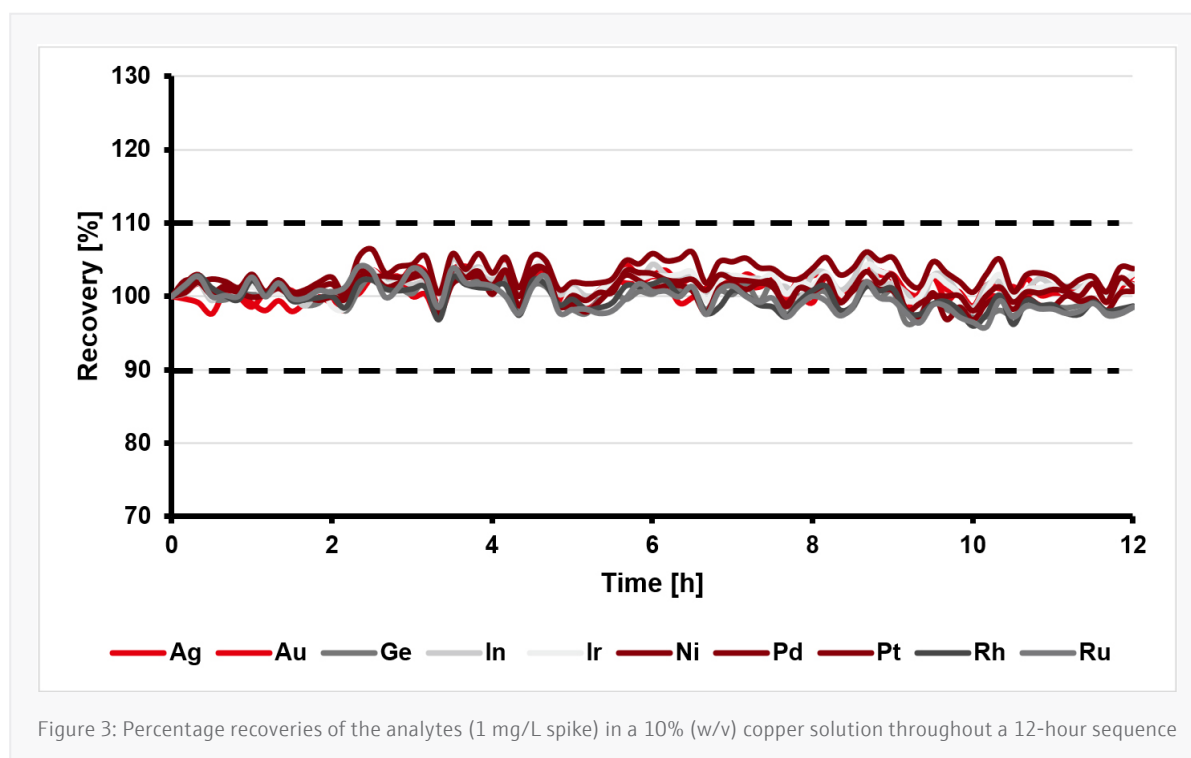
3 ... determined with radial view

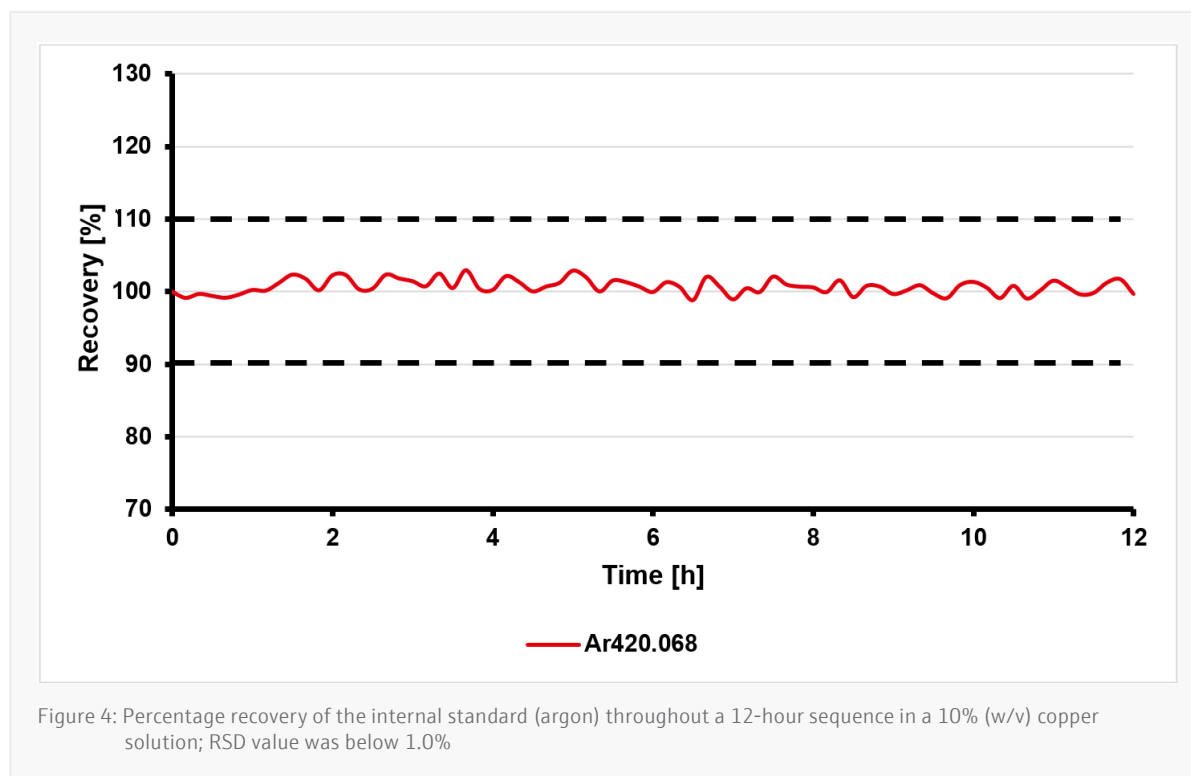
The flexible Dual View PLUS plasma observation system allows for the determination of trace, minor and macro-elements in a single run as done for the different nickel concentrations in the samples (see table 4). This reduces the time for sample preparation by eliminating the pre-dilution of samples.

Due to the natural origin of the ore, the selection of an appropriate internal standard (e.g., Co, In, Sc, Y, etc.) to compensate for matrix effects was hampered. But the aim of this study was to create a method which applies for the whole copper value chain. Therefore, the results were corrected by using the argon emission line at 420.068 nm to cover all matrices with one method. Spiking experiments were carried out to illustrate the applicability of the analytical method. The recoveries were within ± 20% for all elements (Figure 2) illustrating the applicability of the used analytical method.

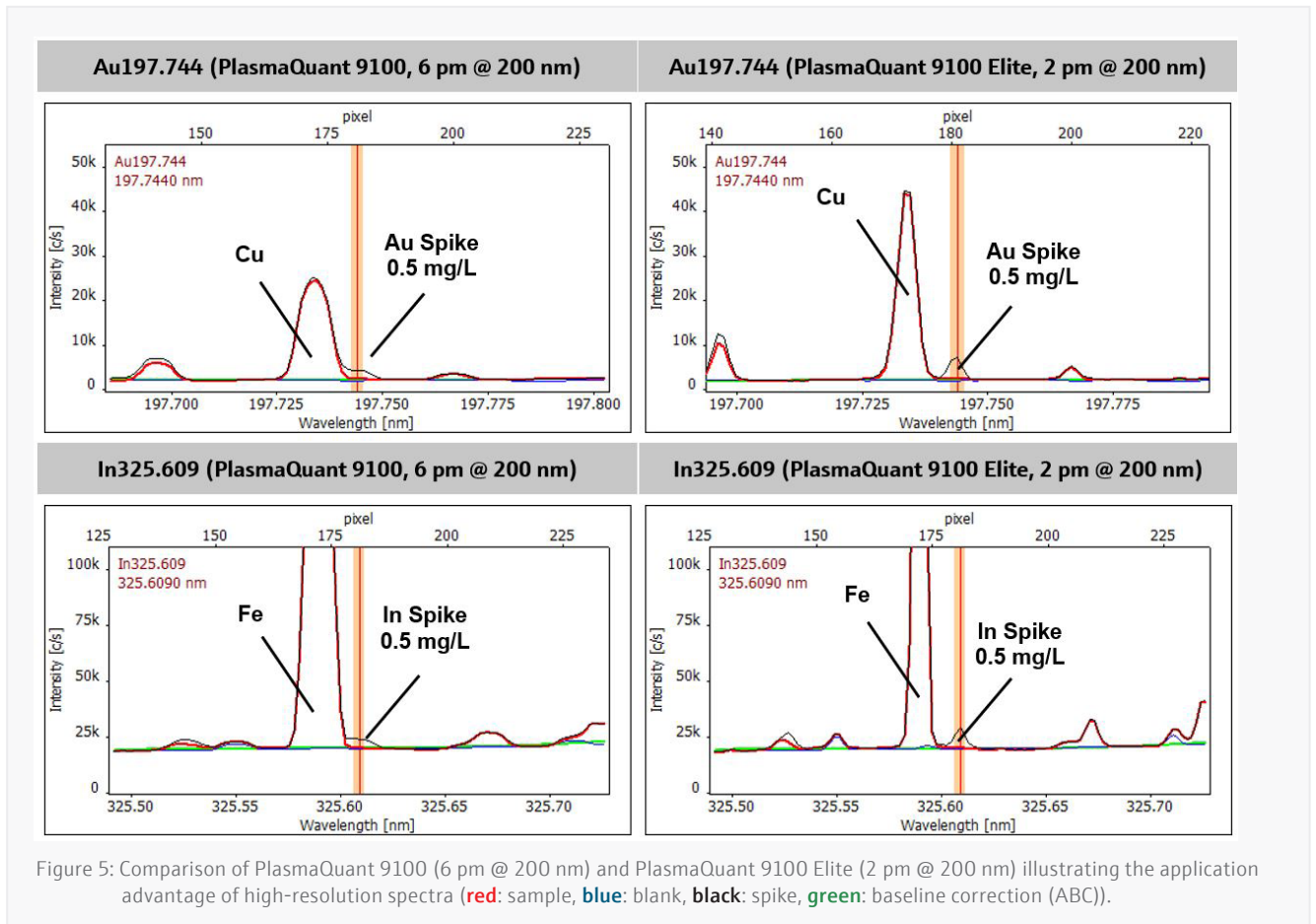


Additionally, the long-term stability was investigated by monitoring the results of the cathode copper sample for 12 hours. In this study, it shows recoveries in the range of $\pm 6\%$ (for analytes, see Figure 3) and $\pm 2\%$ (for internal standard, see Figure 4). Relative standard deviations below 2.0% (for analytes, Figure 3) and 1.0% (for internal standard, Figure 4) indicate a highly stable performance of the instrumentation throughout the 12 hours of measurement.





Interference-free detection of trace signals is a prerequisite for reliable and accurate monitoring of copper materials throughout the entire refinery process. Trace signals can easily be interfered by matrix components. In this regard, high spectral resolution provides well-separated peaks of high definition and therefore circumvents the risk of spectral interferences in the copper analysis. Figure 5 displays a comparison of spectra on the example of gold and indium determined in a copper concentrate sample. The spectra of an instrument with average spectral resolution (left) reveals an insufficient separation of the analytes and the surrounding matrix peaks, which makes it impossible to use this line for reliable quantification. In this case, using an alternative, less sensitive line is inevitable with the consequences of an increased MDL as well as inferior precision and accuracy at the limit concentration. In contrast to the average resolution, the high spectral resolution (right) of the PlasmaQuant 9100 Elite provides a baseline-separated signal for gold and indium. Thus, the sensitive quantification of both elements remains accessible resulting in the lowest possible MDL and highest reliability of the obtained results. The high spectral definition also contributes to an improved sensitivity since it results in larger peak heights and increased readings for a basic three-pixel peak evaluation as commonly applied in ICP-OES.



Summary

In summary, the PlasmaQuant 9100 Elite is well suited for copper and copper ore applications. With its high resolution, high sensitivity, and high plasma robustness the determination of trace elements can be easily performed in such materials. The suitability of the system could be proven with long-term stability and spike recovery tests. The presented method is capable of analyzing copper samples of various matrix compositions.



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