

ICP - Mass Spectrometry

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Determination of Bromine in Ultra-High-Purity Copper Using the NexION 5000 ICP-MS

Introduction

Copper (Cu) is widely used due to its high electrical and thermal conductivity, strong corrosion resistance, excellent

workability and moderate strength. It is one of the few metals that is used most commonly in its pure form, and ultra-pure copper (five to seven nines) specifically is the standard material used in the bonding wire of most integrated circuits and the cables for audio devices. However, the presence of impurities, such as bromine (Br), in high-purity copper reduces its electrical and thermal conductivity to varying degrees and is a limiting factor on the material's quality.

Bromine has two naturally occurring isotopes at m/z 79 and 81, both of which suffer from copper oxide interferences. Coupled with the low ionization efficiency of Br (5%), the determination of bromine in copper is extremely challenging. Therefore, having an ICP-MS which can effectively remove the oxide interferences, prevent additional interferences from forming and be able to accurately quantify at low analyte signals would be a significant advantage, improving the yields of ultra-high-purity copper processing plants.

In this application note, PerkinElmer's NexION® 5000 Multi-Quadrupole ICP-MS was used for the quantification of Br impurities in ultra-high purity copper (approx. 99.999%).

Experimental

Samples and Standards

Ultra-high-purity copper (0.1 g) was dissolved in 2 mL of concentrated HNO₃ (Ultrapure, 68%, Suzhou JINGRUI Chemical Co. Ltd., Suzhou, Jiangsu, China) at room temperature and then diluted to 100 mL with deionized water for analysis.

The method of standard addition (MSA) was used for the analysis of Br in the ultra-high-purity Cu sample solution. Br MSA calibration standards were prepared from 1000 ppm Br (Shanghai Metrology Institute, Shanghai, China). The spiked concentrations were 12.5, 25 and 37.5 µg/L respectively.

Since there was no indium in the sample solution and indium is stable in H₂ Reaction Mode, indium was used as an internal standard.

Instrumentation

The NexION 5000 ICP-MS (PerkinElmer Inc., Shelton, Connecticut, USA) was used for all analyses. Although Br has two isotopes which can be measured, ⁸¹Br has interferences from both ⁶⁵Cu¹⁶O⁺, ⁶³Cu¹⁶OH₂⁺ and from ⁴⁰Ar₂H⁺ generated in the plasma, where the latter two do not react with H₂ and would not be removed with this reaction gas, making low-level Br determination more challenging. Therefore, ⁷⁹Br is the preferred mass for analysis. In order to remove the oxide interference, hydrogen (99.9999%, Baoding North Special Gas Co., Ltd., Baoding, Hebei, China) was used as a reaction gas to mass shift the CuO⁺ interference on Br⁺ and a rejection parameter applied to the cell to prevent side reactions from taking place in the cell.

Results and Discussion

As part of the initial method development, an automated optimization routine in the software was run, which allows the conditions for the lowest BEC for the analyte of interest to be obtained. Using H₂ as a reaction gas, Figure 1a demonstrates the automated cell gas optimization plot which was generated with Syngistix™ for ICP-MS software where 2.1 mL/min was identified as the cell gas flow which delivered the best BECs for ⁷⁹Br. A similar automated software procedure was used to determine the best RPq value (Figure 1b).

Figures 2a and 2b show a product ion scan for the Cu sample solution and a Cu sample solution which had been spiked with 37.5 ppb Br respectively. In Figure 2a, Q1 was set to mass 79 which eliminates all other masses except Br and the CuO interference which both occur at this mass. Q3 was set to scan the product ion formation from mass 79-83. As can be seen in the product ion mass spectrum, the CuO interference, which would have been an overwhelming signal on mass 79, is mass shifted to mass 81. This reaction proceeds rapidly, as evidenced by the disappearance of CuO⁺ at m/z 79 and formation of CuOH₂ at m/z 81. As shown in Figure 2a, ⁶³Cu¹⁶O⁺ is completely eliminated with the use of H₂ in the cell, leaving behind a pure Br signal at m/z 79.

The same experiment was repeated, except the copper solution was spiked with Br and a product ion scan was done from masses 79-83, as shown in Figure 2b. Compared to Figure 2a, a peak is seen at m/z 79, which is due to ⁷⁹Br⁺. Taken together, Figures 2a and 2b demonstrate the effectiveness of eliminating the Cu interference, allowing for interference-free analysis of Br.

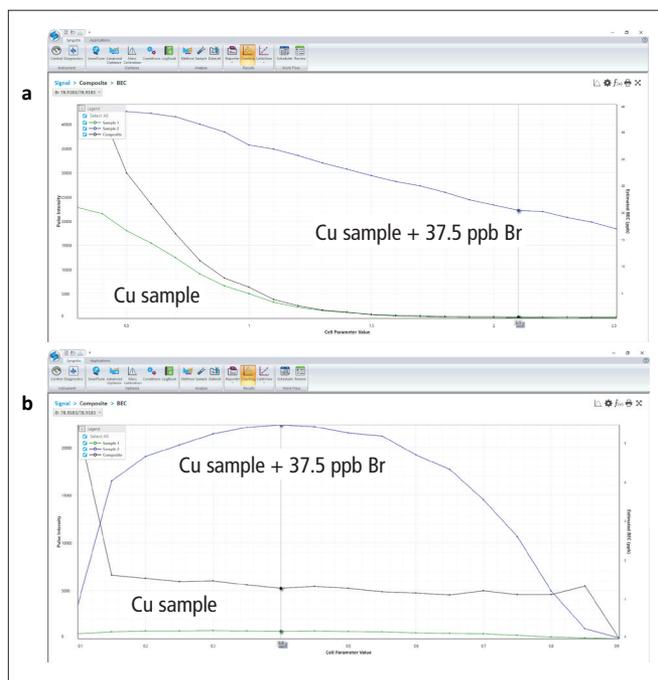


Figure 1. (a) Automated optimization of hydrogen cell gas for ⁷⁹Br in a concentrated Cu solution; (b) automated RPq optimization.

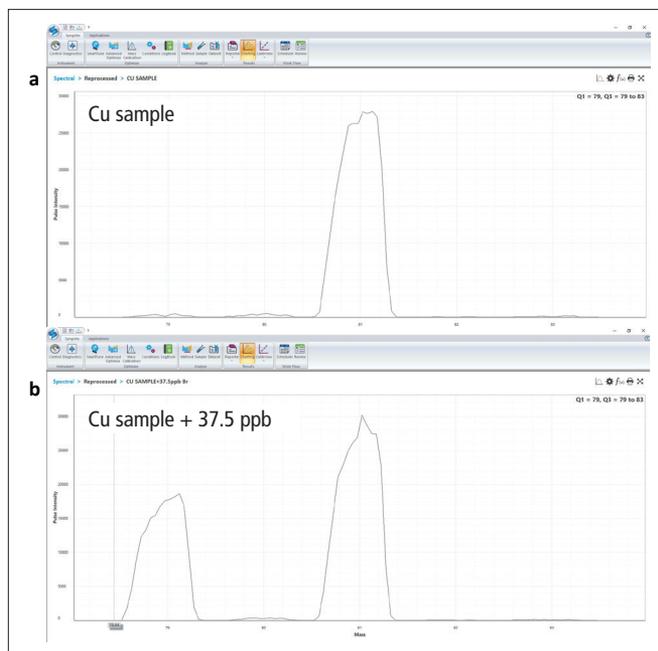


Figure 2. (a) Mass spectrum for Cu in H₂ reaction mode and (b) spectrum for Cu spiked with 37.5 ppb Br in H₂ reaction mode.

Using the method of standard additions, Br was measured in a high-purity copper solution (1000 ppm Cu after dissolution and dilution) and was found to be present at concentrations of 0.122 µg/g. In order to validate these findings, a spike recovery evaluation of a 10 µg/L Br spike was evaluated and determined to be 102%. Figure 3 shows the calibration curve for Br in the highly concentrated copper solution which demonstrates excellent linearity across the defined range ($r^2=0.9998$).

During the same analytical run, indium was used as internal standard and recoveries were all found to be well within $\pm 15\%$ during a four-hour analysis of concentrated copper solutions for Br. A highly concentrated Cu sample solution was analyzed every 20 minutes for Br over a four-hour period (Figure 4) and was found to be within ± 0.026 ppb of the initial reading. This demonstrates the stability of the analysis of Br in concentrated copper solutions over long sample run times using the NexION 5000 ICP-MS.

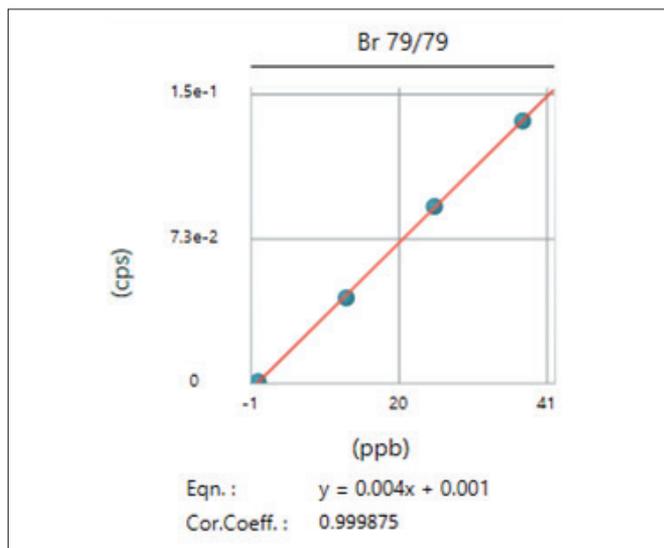


Figure 3. Br Calibration curve.

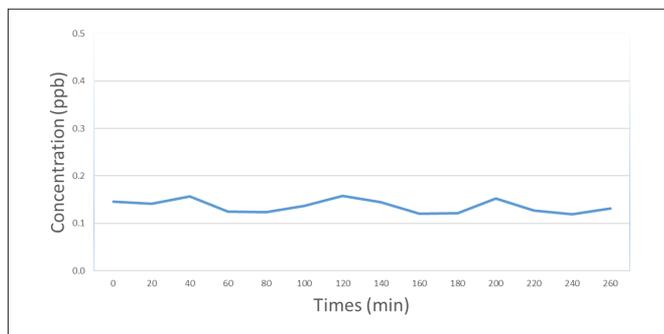


Figure 4. Cu Sample solution run every 20 minutes over four hours.

Conclusion

This application note demonstrates the analysis of low concentration Br impurities in an ultra-pure copper material. In order to address the oxide interferences on the ^{79}Br , hydrogen was added as a reaction gas and was found to deliver analytical results which were both accurate and repeatable, meeting the needs of the copper industry. These results were made possible thanks to:

- The MS/MS capabilities of the NexION 5000 Multi-Quadrupole ICP-MS;
- The ability of the NexION 5000's quadrupole Universal Cell to apply bandpass filtering to prevent side reactions from taking place in the cell;
- The robustness of the NexION 5000 in concentrated and challenging matrices.

Consumables Used

Component	Part Number
Glass Nebulizer	N8152373
Glass Cyclonic Spray Chamber	N8152389
Fixed 2.0 mm Injector UHP Quartz Torch	N8152428
Platinum Sampler Cone	W1033614
Platinum Skimmer Cone	N8161041
Hyper-Skimmer Cone	N8160120
Sample Uptake Tubing	N8145197
Indium Pure Standard, 1000 mg/L	N9303777