Trace Metals Analysis in High Purity Gold Using PlasmaQuant® MS Elite

Introduction

Within the last decades, the demand and production of gold are continuously growing. The biggest demand is in the manufacturing of jewellery with a share of about 50 %. Furthermore, about 10 % of the yearly mined gold is used for manifold applications in the industry. Thanks to its peculiar properties like corrosion, chemical resistance, electrical conductivity and ductility, gold is widely used in electronics industry as material for electrical connections in mass manufactured electronic devices such as circuit boards, integrated chips and semiconductors but also in a variety of novel microelectronic devices like sensors. The well-known biocompatibility of gold has led to its medical use since ancient times. Also a large variety of new applications in high-tech areas, like nanomaterials, are becoming increasingly important.

As an important manufacturing technique, wire bonding is frequently used in microelectronics for the fabrication of conductive tracks in semiconductor applications. Such narrow wires made of gold are used to link one connection pad to another thus completing the electrical connection in an electronic device. Gold remains the most popular material for wire bonding especially when reliable manufacturing and applications in microelectronics packaging are required. High purity gold (> 99.999 %) is indispensable, since even the smallest contaminants can affect the manufacturing processes as well as the electrical and chemical properties of the material, resulting in hard spots, embrittlement, blistering, discoloration and insufficient properties of the manufactured conductors [1].

Challenge

Verification of high purity (5N) Gold

Solution

High sensitivity ICP-MS with iCRC interference management system for routine measurement of trace-element impurities

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Elements to be determined include, depending on materials and processes used, Ag, Pd, Pt, Cu, Cr, Fe, Mg, Ni, Pb, Zn, Be, Ca, and Cd. The here presented application note discusses trace metal determination in high purity 5N gold (> 99.999 % gold) by means of inductively coupled plasma mass spectrometry (ICP-MS).

Instrumentation

A PlasmaQuant® MS Elite ICP-MS was applied for sample analysis. This instrument comprises ReflexION – the patented 3D focusing ion optics enabling unmatched sensitivity of more than 1500 million c/s per mg/L of analyte (^{115}In), while maintaining oxide ratios (CeO^+/Ce^+) below 2 %.

Furthermore, the PlasmaQuant® MS Elite is equipped with the patented integrated Collision Reaction Cell (iCRC) that is able to remove polyatomic ions formed in the plasma, which can interfere the determination of elements like As, Se, Cr, V, and Fe, thus improving their detection limits. All experiments were carried out in a routine analytical laboratory, and not under 'clean room' conditions. The method parameters were optimized using the ICP-MS software's Auto-Optimization routine, which automates setting all ion optics, nebulizer, and plasma parameters. The total sampling time, including the rinse and sample uptake delay, is around two minutes per sample.

Materials and Reagents

Deionized water (18 MΩ·cm, Millipore Milli-Q, Billerica, MA, USA) and high purity nitric and hydrochloric acids (Ultrapur®, Merck, Kilsyth, Victoria, Australia) were used for sample digestion and calibration standard preparations. Before use, all laboratory ware was thoroughly cleaned by acid washing and rinsing.

Sample and Standard Preparation

Calibration and Internal Standards

Two calibration standards, at concentration levels of 1 µg/L and 10 µg/L, were prepared by diluting ICP-MS multi element standard stocks (CCS 2, CCS 4, and CCS 6, Inorganic Ventures, Inc., Lakewood, NJ, USA) with 2 % v/v HNO_3.

An internal standard solution, containing 20 µg/L of Li, Sc, In, Y, Tb, and Bi, was prepared by diluting a 100 mg/L internal standard stock (Inorganic Ventures, Inc., Lakewood, NJ, USA) with 1 % v/v HNO_3. In this work, the internal standard solution was automatically added to the nebulizer through a 'Y piece' using the third channel of the PlasmaQuant® MS Elite sampling pump.

Samples

A gold wire (5N) of approximately 10 g was obtained for analysis and cut into pieces of about 1 g (Au #1 = 1.0828 g, Au #2 = 1.0115 g, Au #3 = 1.0139 g) whilst avoiding contamination by wrapping the wire with Parafilm (Pechiney Plastic Packaging, Menasha, WI 54952, www.parafilm.com). Pre-cleaning of the gold wires was performed by using 20 mL of 25 % aqua regia solution for 15 minutes followed by rinsing with deionized water. The gold pieces were placed into separate 200 mL beakers, each containing 20 mL of aqua regia, and gently heated for roughly 30 minutes until the gold wire dissolved completely. The solutions were heated for a further 15 minutes to reduce the volume of the solution down to 5 mL. After equilibrating to room temperature, the gold solutions were quantitatively transferred into 100 mL volumetric flasks and diluted to the mark with deionized water. In 5 % aqua regia, the gold digest solutions will have total dissolved solids (TDS) content of around 1 % w/v. A preparation blank solution was also prepared with the samples. To ensure matrix effects are at a minimum and excellent precision, accuracy and long term stability is achieved, it is recommended that the TDS of sample solutions be kept at or below 0.2 % w/v. Accordingly, each of the three gold digest solutions were further diluted with 2 % v/v HNO_3 by factor 10. The concentrations of gold in the resulting solutions were equivalent to about 1 g/L.

Analysis considerations

Under conventional hot plasma conditions, argon based interferences can complicate the measurement of calcium and iron at trace level (sub µg/L level). Major isotopes ^{40}Ca and ^{56}Fe are interfered with by $^{40}Ar^+$ and $^{40}Ar^{16}O^+$, respectively. Using iCRC, a small flow of hydrogen gas is introduced at the skimmer cone to attenuate spectroscopic interferences formed in the plasma. In such a way, detection limits of Ca and Fe can achieve sub parts per billion. The PlasmaQuant® MS Elite can be set to operate in a multiple condition with or without the iCRC technique depending on the analyte of interest.

As mentioned earlier, two multi element calibration standards, 1 µg/L and 10 µg/L, were prepared in 2 % HNO_3. To minimize errors in the determination of lead by ICP-MS, the sum of the signals from the three major lead isotopes, that is, ^{206}Pb, ^{207}Pb, and ^{208}Pb, was used. "Interpolated" internal standard correction was the selected mode of correction to automatically adjust calibration and sample solution measurements for matrix and long term drift effects.

Results and Discussion

To determine the measurement accuracy of trace level metals in gold, aliquots of each of the three samples were spiked with the analytes at 0.1 µg/L and 0.5 µg/L levels. The average recovery and standard deviation of both spike levels were very good for the most of analytes even at the 0.1 µg/L spike level (Table 1). The benefits of iCRC mode are clearly shown in the spike recovery of ^{56}Fe: 0.089 µg/L at 0.1 µg/L and 0.532 µg/L at 0.5 µg/L levels. The standard deviations were 0.025 and 0.051 respectively.

Table 1: Averaged recoveries, µg/L, for spikes in gold samples (n = 3).

Analyte	Averaged Spike Recoveries	
	0.1 µg/L (Std Dev.)	0.5 µg/ L (Std Dev.)
iCRC mode		
^{40}Ca	–	1.859 (± 1.318)
^{56}Fe	0.089 (±0.025)	0.532 (± 0.051)
Std mode		
^{9}Be	0.089 (± 0.003)	0.448 (± 0.008)
^{24}Mg	0.085 (± 0.053)	0.455 (± 0.044)
^{52}Cr	0.104 (± 0.010)	0.518 (± 0.003)
^{60}Ni	0.076 (± 0.007)	0.467 (± 0.016)
^{63}Cu	0.101 (± 0.008)	0.504 (± 0.011)
^{66}Zn	0.109 (± 0.093)	0.772 (± 0.082)
^{105}Pd	0.085 (± 0.025)	0.519 (± 0.028)
^{107}Ag	0.082 (± 0.010)	0.521 (± 0.026)
^{111}Cd	0.108 (± 0.003)	0.536 (± 0.004)
^{195}Pt	0.096 (± 0.001)	0.494 (± 0.005)
^{202}Hg	0.093 (± 0.017)	0.497 (± 0.015)
$^{206+207+208}$Pb	0.102 (± 0.003)	0.534 (± 0.049)

Detection limits for this method were calculated as the concentration giving a signal equal to three times the standard deviation of seven replicates of the 0.1 µg/L spike in sample Au #2. The sum of these detection limits is <1 µg/L, which is equivalent to 1 µg/g of Au (or 1 ppm). Thus, it is sufficient to determine trace metal impurities in 99.999 % pure 5N gold even under non cleanroom conditions.

The individual results for the three gold samples as well as the average impurity for each element are listed in Table 2. Furthermore the standard deviation for each element is shown in brackets.

Table 2: Results for all three gold samples and their average.

Analyte	Au #1 (mg/kg)	Au #2 (mg/kg)	Au #3 (mg/kg)	Average (Std Dev.)
iCRC mode				
^{40}Ca	0.6294	2.8792	0.8013	1.437 (± 1.252)
^{56}Fe	0.2566	0.2791	0.2440	0.256 (± 0.018)
Std mode				
^{9}Be	< 0.0050	< 0.0050	< 0.0050	< 0.005
^{24}Mg	< 0.0050	0.0164	0.0672	0.042 (± 0.036)
^{52}Cr	0.1004	0.1040	0.0874	0.097 (± 0.009)
^{60}Ni	< 0.0240	< 0.0240	< 0.0240	< 0.024
^{63}Cu	0.0151	0.0163	< 0.0090	0.016 (± 0.001)
^{66}Zn	0.1384	0.1887	0.1319	0.153 (± 0.031)
^{105}Pd	< 0.0130	< 0.0130	0.0352	0.035
^{107}Ag	0.5201	0.5139	0.5952	0.543 (± 0.045)
^{111}Cd	0.0157	0.0072	0.0082	0.010 (± 0.005)
^{195}Pt	0.0450	0.0393	0.0444	0.043 (± 0.003)
^{202}Hg	< 0.0530	0.0910	< 0.0530	0.091
$^{206+207+208}$Pb	0.0850	0.0220	0.0265	0.045 (± 0.035)

The resulting total trace metal impurities ($\Sigma_{Impurities}$) found in the 5N Gold samples and the calculated % purity are shown in Table 3. On the basis of the ICP-MS results the purity of this 5N gold wire is > 99.9995 %.

Table 3: Calculated purity of gold samples.

Purity	Au #1	Au #2	Au #3	Average
$\Sigma_{Impurities}$ (ppm)	1.9	4.2	2.1	2.8
%Purity of Au	99.9998	99.9996	99.9998	99.9997

Conclusion

The PlasmaQuant® MS Elite has been successfully used for the determination of trace impurities in pure 5N Gold. This work demonstrates the benefits of high sensitivity and iCRC interference management in routinely achieving the detection limits necessary to measure gold purity to five nines (5N). In fact, routinely achieving detection limits to determine contaminates in gold of six nines (6N) purity is not far out of reach and would only require slightly cleaner working conditions.

References

[1] Kinneberg, D. J. ; Williams, S. R.; Agarwal, D. P. ; *Origin and Effects of Impurities in High Purity Gold*. Gold Bulletin, **1998**, 31 (2): 58