Impurity Elements Determination in High Purity Gold by Using LA-ICP-MS

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Abstract. The various impurities in high purity gold directly affect the quality and value of gold, and which concentration is usually ultra-low. The laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS) is a quasi-non-destructive multi-elemental analytical method with low detection limits, high sensitivity and specificity. In this study, we introduce this method to detect impurity elements of 99.999\% high purity gold through optimizing the parameters of laser energy density, repetition rate, and crater diameter. The concentration of 20 impurities were determined based on standard curve method, independently verified by glow discharge mass spectrometry (GD-MS) and inductively coupled plasma mass spectrometry (ICP-MS). The result shows the quantitative method was successfully used to the determination of impurity elements in high purity gold with the benefits of quasi-non-destruction, simplicity, real-time and green.

1. Introduction
High purity gold has a unique financial attribute and is widely used in in energy, environment, electronics and industrial fields [1-3]. The content of impurity elements in high purity gold affect the value of gold significantly, thus, the determination of impurity elements in high purity gold become an indispensable part.

In general, the determination of impurity elements in gold samples mainly includes non-destructive method and destructive method. The X-ray fluorescence spectrometer was used to analysis content of impurity elements in gold according to standards GB/T 18043 [4] as a non-destructive method. However, limited by the low detection, it failed to detect impurity elements in high purity gold. Meanwhile, the destructive methods of determination of impurity elements were used according to standards GB/T 25934 [5] series by using inductively coupled plasma and inductively coupled plasma mass spectrometry. However, destructive method requires complex pretreatment such as extraction and dissolution of samples, which has disadvantages of time-consuming, high cost and a greater risk of sample contamination. It is noteworthy that glow discharge mass spectrometry (GD-MS) as a method for direct solid analysis was widely used, but it also has a large damage of sample. Thus, it is urgently-needed to find a quasi-non-destructive, simple and accurate analytical method for impurity elements in high purity gold.

Herein, a method for the determination of impurity elements in high purity gold based on laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS) was introduced. Laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS) is a new technology which uses focused laser scanning to excite solid samples and inductively coupled plasma mass spectrometry ionization to
analyze the content and distribution of elements in samples. It has the advantages of easy assembly, wide determination range of elements (covering most elements in periodic table), few samples consumption (only a few micrograms), high spatial resolution and sensitivity [6]. Thus, it can be used for micro-area content analysis of samples [7]. These excellent advantages make it great potential applications in geology, materials, metallurgy, archaeology, medicine and biology [8]. Meanwhile, LA-ICP-MS has been widely used in isotope geochemistry and chronology. For instance, age data of the U-Pb and Hf isotope of zircons was obtained at the same location by Zhao et al. [9]. Zhang et al. [10], Becker et al. [11] and McLeod et al. [12] applied LA-ICP-MS to frontier research in biological field. Professor Wang Haizhou, Institute of Iron and Steel, has made a comprehensive study on the element distribution, coating depth and surface microanalysis of LA-ICP-MS in the field of materials science, such as iron and steel, non-ferrous metals and semiconductors [13-15]. To our knowledge, no attention has been paid to use LA-ICP-MS determining impurity elements in high purity gold. In our study, the concentration of 20 impurities were successfully determined based on standard curve method, independently verified by glow discharge mass spectrometry (GD-MS) and inductively coupled plasma mass spectrometry (ICP-MS).

2. Experimental Section

2.1. Instruments
ICAP RQ inductively coupled plasma mass spectrometer (Thermo Fisher), New Wave 213 Nd: YAG laser ablation system (New Wave Research). Sample aerosols produced by laser ablation was transported by carrier helium and mixed with auxiliary gas argon before testing. Element GD glow discharge mass spectrometry (Thermo Fisher), 7700X inductively coupled plasma mass spectrometry (Agilent).

2.2. Samples
99.999% high purity gold samples come from different manufacturers. GSB 04-3312-2016 (Shandong Mokingran Jewelry Co., Ltd) series gold standard and the gold content of series standard sample were 99.9909%, 99.9801%, 99.9488%, 99.892% and 99.8001%.

2.3. Experimental Parameters
The experimental parameters of LA-ICP-MS are shown in table 1.

| LA/Parameters                     | ICP-MS/Parameters        |
|----------------------------------|--------------------------|
| Laser wavelength (nm)            | 213                      |
| Laser energy (J/cm²)             | 1.3-31                   |
| Crater diameter (μm)             | 4-110                    |
| Pulse frequency (Hz)             | 1-20                     |
| Scanning rate (μm/s)             | 10                       |
| XY mobile carrier station (mm x mm) | 100×100             |
| Camera magnification (X)         | 15-60                    |
| Microscopic resolution (μm)      | 2                        |
| Ablation mode                    | Line scanning            |
|                                  | RF power (W)             |
|                                  | Cooling air flow (Ar) (L/min) | 14     |
|                                  | Auxiliary air flow (Ar) (L/min) | 0.8    |
|                                  | Atomization flow (Ar) (L/min) | 1.09   |
|                                  | Residence time (s)       | 0.01    |
|                                  | Signal acquisition mode  | Time-resolved       |
|                                  | Double-ionized (Ba++/Ba)| < 2%    |
|                                  | Oxide (CeO/Ce)           | < 3%    |

2.4. The Methods
20 kinds of impurity elements were tested including magnesium, titanium, chromium, manganese, iron, nickel, copper, zinc, arsenic, ruthenium, rhodium, palladium, silver, cadmium, tin, antimony, iridium, platinum, lead and bismuth. The line scanning mode of laser ablation (LA) was used and
time-resolution quant mode was used to collect and integrate data of inductively coupled plasma mass spectrometer (ICP-MS). In the testing, the baseline intensity signal of the mass spectrum was used as blank, and the mass spectrometric signal intensity of each element was determined simultaneously. The standard curve of each element-intensity is obtained by testing the series gold standard samples, and the content of impurity elements in purity gold was calculated from the standard curve. At least 3 different test points shall be selected for parallel test of each purity gold sample, and the average value shall be taken. The sample was cleaned with ethanol of analytical pure before testing.

3. Results and Discussion

3.1. Optimization of Experimental Conditions
Elemental signal acquisition is based on time-resolved quant mode and integrated method. In the process of integration, the abnormal peak height should be avoided and the interval with uniform component content should be selected for integration. The signal acquisition time of each sample is 90 seconds, and the gas blank is collected for 20 seconds to make background blank before ablation. After ablating completed, the signal lasts for 20 seconds until the signal returns to the blank level, and the difference between the average value of total signal and the average value of background is the net signal value of the analysis sample. Aerosol was ablated by laser and transmitted to inductively coupled plasma mass spectrometer through carrier gas, thus the interaction is complex and depends on many variables of laser, which directly affects the final signal response. To obtain the optimal conditions for the determination, several factors were optimized, such as energy density, repetition rate and crater diameter. In the experiment, a sample of Au ≥ 99.999% high purity gold was used to optimize the experimental conditions. Meanwhile, considering the gold content of the samples were all more than 99.99%, the content of copper and zinc is relatively high in the samples which applied to be used to evaluate the optimum conditions.

3.2. Energy Density
According to the parameters of the instrument, the energy density of 1.3-31 J/cm² was selected for testing. Taking energy density as abscissa and signal intensity as ordinate, the influence of laser energy density on signal intensity was obtained in figure 1a. As shown in figure 1a, when the laser energy density was less than 18 J/cm², the element signal value was low, which means the insufficient energy density leads to less sample transmission and lower signal intensity. It was found when the energy density reaches 18 J/cm², showing the strongest element signal value and the best signal intensity.

To further verify whether 18 J/cm² is the best condition, the precision was tested through relative standard deviation of five measurements. Figure 1b shows the influence of laser energy density on signal precision. It can be seen that the energy density was less than 18 J/cm², the ablation efficiency was low and the signal precision was poor, it can be deduced that the ablation was not uniform enough when the energy intensity was small, which leads to poor uniformity of transmission. While the energy density is greater than 18 J/cm², the signal sensitivity decreased, the reason can be thought a condition occurred of large particle spatter and deposits during transmission, thus the particles are not loaded into ICP or the load exceeds the ICP loading. In summary, 18 J/cm² was chosen for further study.

3.3. Repetition Rate
Similarly, as an important parameter of laser ablation, laser repetition rate also needs to be optimized. Repetition rate of 1, 2, 4, 5, 10, 20 Hz are used in the study. Figure 2a shows the influence of repetition rate on the signal intensity of elements. The result shows rapid increase of the element signal intensity from 1-10 Hz, then remained slowly increase in the range of 10-20 Hz. Hence 10 Hz was chosen the optimal repetition rate for further study. Figure 2b shows the influence of laser repetition rate on signal precision. The result was consistent with the signal intensity.
Figure 1. (a) The effects of laser energy density on signal intensity; (b) the effects of laser energy density on signal precision.

Figure 2. (a) The effects of laser repetition rate on signal intensity; (b) the effects of laser repetition rate on signal precision.

3.4. Crater Diameter
The selection of the crater diameter directly affects the amount of sample injected, thus affecting the signal intensity. The selection of right crater diameter not only ensures the signal response of trace elements, but also avoids the high signal response of minor elements affecting the detection. The effect of the crater diameter was investigated in the range of 4 to 110 μm. It was found the signal intensity increased with the increase of crater diameter, and when the crater diameter in 80 μm the increasing speed slows down (figure 3a). Meanwhile, the influence of crater diameter of on signal precision was shown in figure 3b. Thus, it can be concluded that the optimal crater diameter was 80 μm.
3.5. Results

3.5.1. Detection Limit. Under optimum conditions, the detection limit of 20 kinds of elements was explored. The limits of detection were calculated as the concentrations equivalent to three times the standard deviation of signal intensities obtained with 10 analyses of the helium carrier gas blank. The result was shown in table 2.

**Table 2.** The detection limit of elements.

| Element  | Detection limit (ppm) | Element  | Detection limit (ppm) |
|----------|-----------------------|----------|-----------------------|
| $^{24}\text{Mg}$ | 0.08                  | $^{103}\text{Rh}$ | 0.01 |
| $^{48}\text{Ti}$  | 0.04                  | $^{105}\text{Pd}$ | 0.01 |
| $^{52}\text{Cr}$  | 0.03                  | $^{107}\text{Ag}$ | 0.01 |
| $^{55}\text{Mn}$  | 0.07                  | $^{111}\text{Cd}$ | 0.01 |
| $^{56}\text{Fe}$  | 0.06                  | $^{118}\text{Sn}$ | 0.15 |
| $^{60}\text{Ni}$  | 0.02                  | $^{121}\text{Sb}$ | 0.01 |
| $^{63}\text{Cu}$  | 0.02                  | $^{193}\text{Ir}$ | 0.01 |
| $^{66}\text{Zn}$  | 0.04                  | $^{195}\text{Pt}$ | 0.01 |
| $^{75}\text{As}$  | 0.14                  | $^{208}\text{Pb}$ | 0.01 |
| $^{101}\text{Ru}$ | 0.01                  | $^{209}\text{Bi}$ | 0.01 |

3.5.2. Detection of Elements in High Purity Gold. The linear correlation of each element was obtained by using a series of gold standard samples (GSB 04-3312-2016). As is seen in table 3, the correlation of each element was more than 0.99 for this method which means the good method applicability.

A series of 99.999% high purity gold samples were determined, and the results of the five parallel measurements of a high purity gold sample were shown in table 4. Table 4 shows the relative standard deviation of each element was less than 13.2%. Notably, the relative standard deviation of Ni, Ru and Pb were more than 10%, but considering the content of the three elements belongs to ultra-trace, the RSD less than 20% was considered reasonable. In summary, this method has good precision.

3.5.3. Comparision between LA-ICP-MS and Other Analytical Methods. To verify the feasibility of this method, the comparision with glow discharge mass spectrometry (GD-MS) and inductively coupled plasma mass spectrometry (ICP-MS) were used, and the results were shown in table 5. As is shown in table 5, the results of the three methods were close to each other. Notably, the content of
impurity elements determined by GD-MS was relatively low, which may be explained to GD-MS adopts the calibration curve designed by the system not the real gold standard sample which causing some deviation with the results of LA-ICP-MS and ICP-MS. In generally, for the total content of impurity elements measured, the results of the three methods were similar. Thus, the method determination of impurity elements in high purity gold using LA-ICP-MS was feasible.

Table 3. Linear correlation of standard curve.

| Element | R-square value | Element | R-square value |
|---------|----------------|---------|----------------|
| $^{24}\text{Mg}$ | 0.9913 | $^{103}\text{Rh}$ | 0.9973 |
| $^{48}\text{Ti}$ | 0.9964 | $^{105}\text{Pd}$ | 0.9964 |
| $^{52}\text{Cr}$ | 0.9972 | $^{107}\text{Ag}$ | 0.9991 |
| $^{55}\text{Mn}$ | 0.9965 | $^{111}\text{Cd}$ | 0.9953 |
| $^{56}\text{Fe}$ | 0.9942 | $^{118}\text{Sn}$ | 0.9986 |
| $^{60}\text{Ni}$ | 0.9987 | $^{121}\text{Sb}$ | 0.9987 |
| $^{63}\text{Cu}$ | 0.9991 | $^{193}\text{Ir}$ | 0.9969 |
| $^{66}\text{Zn}$ | 0.9976 | $^{195}\text{Pt}$ | 0.9991 |
| $^{75}\text{As}$ | 0.9991 | $^{208}\text{Pb}$ | 0.9989 |
| $^{101}\text{Ru}$ | 0.9968 | $^{209}\text{Bi}$ | 0.9987 |

Table 4. The results of sample to be determined.

| Element | Average of 5 measurements (ppm) | RSD (%) |
|---------|---------------------------------|---------|
| $^{24}\text{Mg}$ | 0.0620 | 4.1 |
| $^{48}\text{Ti}$ | 0.0391 | 8.4 |
| $^{52}\text{Cr}$ | 0.0606 | 5.1 |
| $^{55}\text{Mn}$ | <0.07 | / |
| $^{56}\text{Fe}$ | 0.9578 | 2.4 |
| $^{60}\text{Ni}$ | 0.0577 | 10.2 |
| $^{63}\text{Cu}$ | 0.1020 | 5.3 |
| $^{66}\text{Zn}$ | 0.2695 | 2.5 |
| $^{75}\text{As}$ | <0.13 | / |
| $^{101}\text{Ru}$ | 0.0253 | 13.2 |
| $^{103}\text{Rh}$ | 0.0049 | 9.2 |
| $^{105}\text{Pd}$ | 0.0863 | 7.6 |
| $^{107}\text{Ag}$ | 0.8014 | 4.2 |
| $^{111}\text{Cd}$ | <0.008 | / |
| $^{118}\text{Sn}$ | <0.14 | / |
| $^{121}\text{Sb}$ | 0.0120 | 10.2 |
| $^{193}\text{Ir}$ | 0.1150 | 5.6 |
| $^{195}\text{Pt}$ | 0.0945 | 8.5 |
| $^{208}\text{Pb}$ | 0.0125 | 12.1 |
| $^{209}\text{Bi}$ | 0 | / |
| Sum | 3.0486 | / |
Table 5. The results of 3 different analytical methods.

| Element | LA-ICP-MS (ppm) | GD-MS (ppm) | ICP-MS (ppm) |
|---------|-----------------|-------------|-------------|
| $^{24}\text{Mg}$ | 0.0620 | <0.005 | <0.01 |
| $^{48}\text{Ti}$ | 0.0391 | <0.005 | <0.01 |
| $^{52}\text{Cr}$ | 0.0606 | 0.0610 | <0.01 |
| $^{55}\text{Mn}$ | <0.07 | <0.005 | 0.0801 |
| $^{56}\text{Fe}$ | 0.9578 | 0.7800 | 1.0345 |
| $^{60}\text{Ni}$ | 0.0577 | 0.0460 | 0.0681 |
| $^{63}\text{Cu}$ | 0.1020 | 0.0640 | 0.1124 |
| $^{65}\text{Zn}$ | 0.2695 | 0.1900 | 0.3184 |
| $^{75}\text{As}$ | <0.13 | <0.005 | 0.0208 |
| $^{101}\text{Ru}$ | 0.0253 | 0.0090 | <0.01 |
| $^{103}\text{Rh}$ | 0.0049 | <0.005 | <0.01 |
| $^{105}\text{Pd}$ | 0.0863 | 0.0550 | 0.1417 |
| $^{107}\text{Ag}$ | 0.8014 | 0.9500 | 1.0316 |
| $^{110}\text{Cd}$ | <0.008 | <0.005 | 0.0211 |
| $^{118}\text{Sn}$ | <0.14 | <0.005 | 0.0412 |
| $^{121}\text{Sb}$ | 0.0120 | <0.005 | 0.0210 |
| $^{193}\text{Ir}$ | 0.1150 | 0.1700 | 0.1440 |
| $^{195}\text{Pt}$ | 0.0945 | 0.1700 | 0.1234 |
| $^{208}\text{Pb}$ | 0.0125 | <0.005 | <0.01 |
| $^{208}\text{Bi}$ | 0 | <0.005 | 0 |

Sum 3.0486 2.5450 3.2183

Note: the sum was calculated according to the detection limit of not detected elements.

4. Conclusion
In summary, a method for the determination of impurity elements in purity gold by laser ablation inductively coupled plasma mass spectrometry was developed. In the experiment, the optimum experimental conditions of laser energy density, repetition rate, and crater diameter were 18 J/cm², 10 Hz and 80 μm respectively. Under the optimum conditions, the detection limit and linear correlation of standard curve of impurity elements were investigated. By comparing the results of 99.999% high purity sample by different analytical methods, it was found this method has good applicability to impurity elements in high purity gold samples. Thus, a green, real-time and quasi-non-destructive analytical method was developed.

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