Proceedings of the 2nd International Conference on Green Energy, Environment and Sustainable Development (GEESD2021), D. Dobrotă and C. Cheng (Eds.)

doi:10.3233/ATDE210308

Uncertainty Evaluation for Determination of Gold in High-Purity Gold by LA-ICP-MS

Boling HUANG[a,b,1], Xuan WANG[a,b], Tingting YANG[a,b], Jiani SHEN[a,b], Qingzheng MA[a,b], Yong ZHU[a,b], Lansen LI[a,b] and Xihan YANG[a,b]
[a] *Chongqing Academy of Metrology and Quality Inspection, Chongqing 401123, China*
[b] *National Jewelry Testing Center (Chongqing), Chongqing 401123, China*

Abstract. Laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS) is a new analytical method developed in recent years. The LA-ICP-MS is a quasi-non-destructive multi-elemental analytical method with low detection limits, high sensitivity and specificity. In this study, this method is applied to detecting high-purity gold. The micro-region information of high-purity gold can be analysed, and the original position information of the sample can be obtained in real time and accurately. In this study, the content of impurity elements in high-purity gold were determined by LA-ICP-MS, and the accuracy and reliability of the test results were improved by calculating the uncertainty. According to the test and analysis, the gold content of the high purity gold sample is (999.995 ± 0.003) ‰, so the gold content of the sample is more than 999.99 ‰. The result shows that the LA-ICP-MS has the advantages of fast, accurate and green, which is conducive to the rapid development of jewellery industry technology, and puts forward guiding suggestions for the production development direction, and promotes the green and healthy development of jewellery industry.

Keywords. LA-ICP-MS, green development, jewellery industry

1. Introduction

High-purity gold means that the mass fraction of gold is not less than 999.99‰, or the total mass fraction of impurity elements is not more than 10×10^{-6} [1-2]. In the raw materials of gold or gold alloy used for lead, target and solder in electronic industry, if 999.9‰ gold is replaced by high purity gold, the solderability, semiconductor properties and stability of the materials will be greatly improved [2], and the high-purity gold is widely used in energy, environment, electronics and industrial fields [3-5].

Laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS) is a new analytical method developed in recent years. In this method, the sample surface is eroded, sputtered and evaporated by focused laser beam to form aerosol [6-7]. The trace elements in the sample can be obtained by mass spectrometry, and this method is widely used in geology, biological, materials, archaeology fields [8-11].

A method for the determination of impurity elements in gold jewellery based on laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS) is

[1] Corresponding Author, Boling HUANG, Chongqing Academy of Metrology and Quality Inspection, Chongqing 401123, China; Email: hbl_hot@126.com.

introduced. Laser ablation inductively coupled plasma mass spectrometry (ICP-MS) is a new technology which uses focused laser scanning to excite solid samples and then ionize them by inductively coupled plasma mass spectrometry (ICP-MS) to analysis the content and distribution of elements in samples. It has the advantages of easy assembly, wide range of elements (covering most of the elements in the periodic table), less samples (only a few micrograms), high spatial resolution, high sensitivity, and it can be used to analysis the micro area information of the sample and obtain the in-situ information of the sample in real time and accurately.

2. Experiment

2.1. Samples

The samples of 999.99‰ high-purity gold were selected for the experiment. The surface of the samples was smooth without obvious scratch, cavity and other defects. GSB 04-3312-2016 series gold standard materials.

2.2. Instrument and Equipment

This research used the iCAP RQ inductively coupled plasma mass spectrometer (Thermo Fisher) and the New Wave 213 nm Nd: YAG laser ablation system (New Wave Research).

2.3. Methods

Samples were sampled in accordance with T/CST 2-2020 and ISO 11596-2008 [12-13]. The gold standard materials and the high-purity gold samples to be detected fixed to the laser sample bin. Try to ensure that the samples and the standard materials have been in the same horizontal position. The test area of samples should to be pre-detection to ensure the flatness and clean. Under the selected operating conditions, after the baseline was stabilized, the sample signal acquisition was started. The signal strength of the baseline was blank, and the mass spectrometry signal strength of the trace element is detected. The impurity elements contents of the samples were calculated according to the standard curve, and then acquired gold content of the high purity gold samples according to the difference. At least 3 different test points shall be selected for parallel test of each purity gold sample, and the average value shall be taken.

3. Results

3.1. Gold Contents

In order to evaluate the uncertainty, we select a high purity gold sample for the detection. The content detection results of the sample are shown in table 1. It can be seen from the table that the test results of other elements are less than the detection limit except the elements of chromium, iron, silver, tin and iridium. It will be regarded as zero in the difference calculation if the impurity element of the test result was less than the detection

limit. The impurity elements of the samples are mainly chromium, iron, silver, tin and iridium, and the total amount of impurity elements is 5.062 mg/kg. According to the difference method, the gold content of the sample is 999.995‰.

3.2. Uncertainty

In order to reasonably give the measured value dispersion, the parameters associated with the test results can measure the quality level of the test results, and improve the accuracy and reliability of the test results. In order to calculate the uncertainty of the result, it was needed to determine the source of the uncertainty in the process of measurement, establish the model, and deduce the combined standard uncertainty and expanded uncertainty. Considering the content of Cr, Fe, Ag, Sn and Ir in the sample were higher than the detection limit, the uncertainty of these five elements should be calculated.

3.2.1. Mathematical Model

Using LA-ICP-MS to determine the content of impurity elements in high purity gold under selected parameters, the content results of each impurity element to be tested can be expressed by the following formula:

$$I = a + b\omega \tag{1}$$

Table 1. The results of the sample.

Element	Results (mg/kg)	Detection limit (mg/kg)	Element	Results (mg/kg)	Detection limit (mg/kg)
Mg	0.097	0.682	Ti	0.014	1.021
Cr	0.194	0.078	Mn	0.058	0.159
Fe	2.175	0.958	Ni	0.012	0.202
Cu	0.014	0.198	Zn	0.037	0.780
As	0.030	0.454	Ru	0.001	0.031
Rh	0.000	0.005	Pd	0.019	0.061
Ag	2.284	0.140	Cd	0.026	0.036
Sn	0.401	0.192	Sb	0.006	0.021
Ir	0.008	0.003	Pt	0.002	0.009
Pb	0.017	0.109	Bi	0.000	0.007

In the formula, I stand for signal intensity, a stands for intercept of calibration curve, b stands for slope of calibration curve, ω stands for mass fraction of elements to be measured (mg/kg).

3.2.2. Source Analysis of Uncertainty

According to the experimental method and mathematical model, the sources of uncertainty in the determination of high purity gold by LA-ICP-MS are as follows:

$u_{rel}(C)$: Relative standard uncertainty introduced by reference material.

$u_{rel}(\omega_C)$: Relative standard uncertainty introduced by standard curve.

$u_{rel}(A)$: Relative standard uncertainty introduced by repeatability.

3.2.3. Relative Standard Uncertainty Introduced by Reference Material

The relative standard uncertainty of the measured element of the reference material can be approximated by the root mean square calculation of the relative standard uncertainty of the measured element of each standard material.

$$u_{rel}(C) = \sqrt{\frac{\sum_{i=1}^{n} u_{rel}(C_i)^2}{n}} \tag{2}$$

In the formula, $u_{rel}(C_i)$ stands for relative standard uncertainty of the element to be measured for the *i* standard material.

The standard uncertainty u of the five test elements of Cr, Fe, Ag, Sn and Ir in the standard sample is checked by the standard material certificate, and the relative standard uncertainty of each test element is calculated using the above formula. The results are shown in table 2.

3.2.4. Relative Standard Uncertainty Introduced by Standard Curve

In this experiment, five gold standard samples were used. The signal intensity was measured by laser ablation inductively coupled plasma mass spectrometry. Each point was measured three times, and the samples were measured 10 times at the same time. The least square method was used for fitting.

According to JJF 1059.1-2012 and GB/T 27418-2017, the standard uncertainty generated by the linear fitting of the calibration curve for the determination of each element to be measured in the sample is:

$$u(\omega_C) = \frac{S_R}{b}\sqrt{\frac{1}{P} + \frac{1}{n} + \frac{\left(\overline{\omega} - \overline{\omega_C}\right)^2}{\sum_{i=1}^{n}\left(\omega_{Ci} - \overline{\omega_C}\right)^2}} \tag{3}$$

In the formula, S_R stands for residual standard deviation, $\overline{\omega_C}$ stands for average of calibration contents of calibration curve, n stands for measurement times of reference materials (n=15), *P* stands for measurement times of the sample (*P*=10).

According to the following formula, the relative standard uncertainty of calibration curve linear fitting for the determination of each element in the sample can be obtained:

$$u_{rel}(\omega_C) = \frac{u\left(\omega_C\right)}{\overline{\omega}}$$

The relative standard uncertainty of each element to be measured is shown in table 3.

Table 2. Content and uncertainty of reference materials.

Element	1		2		3		4		5		$u_{rel}(C)$
	Content (mg/kg)	u	Content (mg/kg)	u	Content (mg/kg)	u	Content (mg/kg)	u	Content (mg/kg)	u	
Cr	0.11	0.04	1	0.5	3	0.5	5	0.5	10	0.5	0.291
Fe	0.29	0.09	5	0.5	10	0.5	22	1	43	1.5	0.150
Ag	0.36	0.11	6	0.5	16	0.5	54	1.5	150	5	0.144
Sn	0.005	0.01	4	0.5	10	0.5	21	1	39	1.5	0.897
Ir	0.029	0.058	2	0.5	2	0.5	7	0.5	11	1	0.910

Table 3. Statistical parameters of the standard working curve of the five elements to be tested.

Element	Content of sample (mg/kg)	a	b	S_R	$u(\omega_C)$ (mg/kg)	$u_{rel}(\omega_C)$
Cr	0.193	16	851	390	0.109	0.564
Fe	2.173	1109	799	1277	0.354	0.163
Ag	2.283	5568	3790	21288	1.160	0.508
Sn	0.406	1884	1586	3286	0.491	1.209
Ir	0.007	2991	18607	13650	0.181	24.755

3.2.5. Relative Standard Uncertainty Introduced by Repeatability

Under the same conditions, the sample was repeatedly determined for 10 times, and the signal strength and related statistical results of the five elements, including Cr, Fe, Ag, Sn and Ir, were obtained, as shown in table 4.

The standard deviation of 10 measurements was obtained by Bessel formula. The relative standard uncertainty was obtained according to formulas $u(A) = \frac{S_A}{\sqrt{n}}$ and $u_{\mathrm{rel}}(A) = \frac{U(A)}{\overline{\omega}}$. The calculation results were shown in table 4.

3.2.6. Uncertainty Combination

The relative standard uncertainty of the standard materials, introduced by the calibration curve, and the introduced by the repeatability of the sample were calculated to combined relative uncertainty:

$$u_{\mathrm{Crel}}(\omega) = \sqrt{u_{\mathrm{rel}}(C)^2 + u_{\mathrm{rel}}(\omega_C)^2 + u_{\mathrm{rel}}(A)^2} \tag{4}$$

Calculated by the above formula, the combined relative uncertainty of each element to were obtained, and the combined standard uncertainty was calculated according to the combined relative uncertainty, the calculation results were shown in table 5.

$$u_C(\omega) = u_{Crel}(\omega) \times \overline{\omega} \tag{5}$$

Table 4. Repeated determination content of the five elements and related statistical results.

	Cr (mg/kg)	Fe (mg/kg)	Ag (mg/kg)	Sn (mg/kg)	Ir (mg/kg)
1	0.077	1.576	2.407	0.516	0.008
2	0.387	2.78	2.34	0.43	0.009
3	0.124	2.224	2.478	0.376	0.007
4	0.108	2.54	2.18	0.408	0.008
5	0.062	2.68	2.284	0.398	0.007
6	0.216	2.329	2.314	0.322	0.004
7	0.417	2.344	2.232	0.451	0.007
8	0.216	0.963	2.068	0.355	0.006
9	0.155	2.575	2.359	0.494	0.006
10	0.17	1.716	2.169	0.312	0.011
Ave	0.193	2.173	2.283	0.406	0.007
SD	0.122	0.578	0.123	0.068	0.002
Standard uncertainty	0.039	0.183	0.039	0.022	0.001
Related standard uncertainty	0.199	0.084	0.017	0.053	0.082

Table 5. The combined relative uncertainty and the combined standard uncertainty of the elements to be measured.

Element	Content of sample (mg/kg)	Combined relative uncertainty	Combined standard uncertainty
Cr	0.193	0.665	0.128
Fe	2.173	0.237	0.515
Ag	2.283	0.528	1.206
Sn	0.406	1.506	0.612
Ir	0.007	24.772	0.181

Combined the standard uncertainty of Cr, Fe, Ag, Sn and Ir:

$$u_{Csum}(\omega) = \sqrt{0.128^2 + 0.515^2 + 1.206^2 + 0.612^2 + 0.181^2} = 1.464\ mg/kg$$

Taking 95% confidence level, including factor k = 2, the expanded uncertainty was as follows:

$$U_{sum}(\omega) = u_{Csum}(\omega) \times 2 = 2.928\ mg/kg$$

3.3. Content of the High-Purity Gold

Combined the expanded uncertainty and the content of sample, the gold content in the sample can be expressed as follows:

$$\omega_{Au} = (999.995 \pm 0.003)‰$$

4. Conclusion

In this study, the content of impurity elements in high-purity gold were determined by LA-ICP-MS, and the accuracy and reliability of the test results were improved by calculating the uncertainty. According to the test and analysis, the gold content of the high purity gold sample is (999.995 ± 0.003)‰, so the gold content of the sample is more than 999.99‰. The result shows that the LA-ICP-MS has the advantages of fast, accurate and green, which is conducive to the rapid development of jewellery industry technology, and puts forward guiding suggestions for the production development direction, and promotes the green and healthy development of jewellery industry.

References

[1] GB/T 25933-2010 *High-Purity Gold* (Beijing: National Standard Press).
[2] Tan Z, Chen J, Wen M, et al. 2019 Review on study of high purity gold sputtering target material used in electronics industry *Precious Metals* **40** (2) 83-87+94.
[3] Zhang B, Wu Y, Zhang K, et al. 2017 Research status and prospect on preparation of high-purity gold and silver *Rare Metals and Cemented Carbides* (6) 1-4.
[4] Zhang J, Xie H, Yang A, et al. 2015 Status and prospect of preparative methods for high-purity gold *Precious Metals* **36** (3) 81-86.
[5] Niu C, Cao M, Wu X, et al. 2018 Extraction process and ICP-OES determination of impurities in high purity gold *China Quality Supervision*.
[6] Yang X, Liu Y, Li N, et al. 2019 Determination of 10 impurities in high purified hafnium by laser ablation inductively coupled plasma mass spectrometry *Spectroscopy and Spectral Analysis* **39** (2) 571-576.
[7] Wang X, Yang T, Huang B, et al. 2019 Impurity elements determination in high purity gold by using LA-ICP-MS *Gemology & Technology* 398-401.
[8] Liu Y, Hu Z, Li M, et al. 2013 Application of LA-ICP-MS in element analysis of geological samples *Chinese Science Bulletin* **58** (36) 3753-3769.
[9] Hu S, Zhang S, Hu Z, et al. 2007 Detection of multiple proteins on one spot by laser ablation inductively coupled plasma mass spectrometry and application to immuno- microarray with element-tagged antibodies *Analytical Chemistry* **79** (3) 923-9.
[10] Zoriy M V, Dehnhardt M, Reifenberger G, et al. 2006 Imaging of Cu, Zn, Pb and U in human brain tumor resections by laser ablation inductively coupled plasma mass spectrometry *International Journal of Mass Spectrometry* **257** (1-3) 27-33.
[11] Hutchinson R W, Cox A G, Mcleod C W, et al. 2005 Imaging and spatial distribution of beta-amyloid peptide and metal ions in Alzheimer's plaques by laser ablation-inductively coupled plasma-mass spectrometry *Analytical Biochemistry* **346** (2) 225.
[12] T/CST 2-2020 Gold adornment alloys—Determination of Multi-element contents—Laser Ablation-inductively Coupled Plasma Mass Spectrometry.
[13] ISO 2008 ISO/TC 174: Jewellery and precious metals. Jewellery—Sampling of precious metal alloys for and in jewellery and associated products.