DOI 10.1007/s11595-009-4608-5

Determination of Trace Elements in High Purity Gold by High Resolution Inductively Coupled Plasma Mass Spectrometry

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Abstract: Trace elements were determined in high purity gold by high resolution inductively coupled plasma mass spectrometry (HR-ICP-MS). Sample were decomposed by aqua regia. To overcome some potentially problematic spectral interference, measurements were acquired in both medium and high resolution modes. The matrix effects due to the presence of excessive HCl and Au were evaluated. The optimum conditions for the determination was tested and discussed. The standard addition method was employed for quantitative analysis. The detection limits range from 0.01μg/g to 0.28μg/g depending on the elements. The method is accurate, quick and convenient. It has been applied to the determination of trace elements in high purity gold with satisfactory results.

Key words: high purity gold; trace elements; high resolution inductively coupled plasma mass spectrometry; spectral interferences

1 Introduction

The industrial and technical important of high purity gold has increased in recent years with the development of advanced electronic devices. The determination of trace elements in high purity gold is a very important procedure for the financial markets, the jewelry business and the electronics industry. Thus, a sensitive, rapid and reliable analytical method for analysis of trace elements in high purity gold is required. Several analytical techniques, including atomic absorption spectrometry (AAS) method[1, 2], inductively coupled plasma atomic emission spectrometry (ICP-AES)[3, 4], and inductively coupled plasma mass spectrometry (ICP-MS)[5, 7] have been applied for trace impurities determination in high purity gold. However, AAS method is not appropriate for multi-element routine analysis because AAS instrumentation is typically constructed as a mono-element method. ICP-AES and ICP-MS usually require the separation of matrix/constituent elements to minimize interferences and signal suppressions. Chemical separation of the matrix from all other minor or trace constituents is impossible in a single step. Matrix separation depends on high selective reactions[8, 9].

High-resolution inductively coupled plasma mass spectrometry (HR-ICP-MS) is capable of resolving many plasma-, water-, and matrix-based polyatomic interferences, and the technique has been used for the successful determination of elements which are subject to spectral interference in complex matrices[10]. HR-ICP-MS is characterized by its high sensitivity, low detection background, and the possibility of separating analyte signals from spectral interferences using higher mass resolution techniques[11]. Nakane *et al* reported the comparative analysis of high-purity metal oxide by ICP-MS with high and low mass resolution[12]. Good analytical results and low detection limits were obtained using the high resolution instrument.

Since the matrix effects for ICP-MS were more serious than those for ICP-AES, many studies were reported in detail. Various mechanisms of matrix effects were proposed for ICP-QMS. However, only in a few HR-ICP-MS studies, the matrix effects have been investigated. For high purity gold, reports on the matrix effects for HR-ICP-MS has not found in the literatures.

14 trace elements including Ag and Fe in high purity gold were determined, whose sample was dissolved, through high resolution inductively coupled plasma mass spectrometry (HR-ICP-MS). Most of the spectral interferences could be overcome by using different resolution

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(Received: June 6,2008; Accepted: Oct. 12, 2008)

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Funded by the Hunan Provincial Natural Science Foundation of China(No. 05JJ40017) and Hunan Provincial Education Department of China (No. 07C029，08C260)

mass spectrometry mode. The effects of HCl and gold matrix on HR-ICP-MS were discussed in detail. The correction for matrix effects was made using Sc, Rh and Bi as internal standards, and the trace elements in several commercially available high purity gold were determined.

2 Experimental

2.1 Instrumentation

HR-ICP-MS of the micromass plasma trace 2 (Micromass Ltd, Manchester, England) was used for the determination of trace elements, which is equipped with a double focusing magnetic sector mass spectrometer of reversed Nier-Johnson geometry. An accelerating voltage was applied to the interface region between the sampler and the skimmer to provide ion kinetic energies sufficient to pass through the mass spectrometer. Variable resolution settings can be adjusted from 400 to 10000 depending on the analytical problem. For the comparison of analytical results, A HP4500 series300 ICP-MS (Hewlett Packard, USA) was used. Typical operating conditions for the HR-ICP-MS are listed in Table 1.

Table 1 Instrumental conditions for the HR-ICP-MS

R_f power	1350 W
Coolant gas flow	14.5 L/min
Auxiliary gas flow	0.9 L/min
Nebuliser gas flow	1.2 L/min
Sampling cone	Nickel, 1.1 mm orifice diameter
Skimmer cone	Nickel, 0.8 mm orifice diameter
Ion sampling depth	11 mm
Sample uptake rate	0.25 mL/min
Dwell time	20 ms
Accelerating voltage	6 kV
Resolution	400-10000
Scanning mode	Peak hopping transient
Ion lens setting	Adjusted to obtain maximum signal intensity

2.2 Standards and reagents

All reagents used were prepared from analytical-grade/specpure chemicals (National Standards of China). Ultrapure water (specific resistance above 18.0 MΩ cm) from a Milli-Q deionization unit (Millipore, Milli-Q SP) was used throughout the experiment. Aqua regia was used to dissolve gold samples.

Single element calibration solutions were prepared from 1000 μg/mL stock solutions of Mg, Ti, Cr, Mn, Fe, Ni, Cu, Zn, As, Pd, Ag, Sn, Sb and Pb in 10% HNO_3 by dilution with ultrapure water. The same procedure was followed for the preparation of the working solution to be used as the internal standard for mass spectrometric determinations. Multi-element standard solutions were prepared from single element stock solutions. These solutions were freshly prepared.

The purification of HNO_3 and HCl were carried out by the recycled sub-boiling distillation of analytical grade acid three times. The glass containers were used throughout the work, and were cleaned by immersion in concentrated HNO_3 and concentrated HCl overnight, then steaming successively with HNO_3 and water vapor for 8 h.

2.3 Analytical procedures

A 0.05 g high purity gold sample was dissolved in 6 mL aqua regia under gentle heating on the sand bath. The solution obtained was evaporated to near dryness, dissolved in 6 mol/L HCl, transferred into a 100 mL volumetric flask and made up with 6 mol/L HCl. The solution was diluted 10 times with ultrapure water so that gold was about 500 mg/L, and the solution was led into the HR-ICP-MS. Process a reagent blank in the same way.

3 Results and Discussion

3.1 Selection of isotopes and spectral interferences

The increase of the mass resolution leads to a reduction of the number of transmitted ions, as a consequence, the sensitivity is reduced to a certain extent. Therefore, to measure the trace impurities, we must use sufficient resolving power enough to separate analyte ion peaks from interfering polyatomic ion peaks, but not more. The measured peaks to determine contents in the samples were isotopes whose abundances are maximum, or isotopes which are not overlapped by the polyatomic or doubly charged ion peaks of matrix elements (Au, Cl and O) and Ar. Mass spectra (m/z=1-280) were obtained in three kinds of resolution modes: low resolution mode (LRM, $m/\Delta m=400$), medium resolution mode (MRM, $m/\Delta m=4000$), high resolution mode (HRM, $m/\Delta m=8000$). The isotopes determined are shown in Table 2.

In ICP-MS, most of the elements determined may suffer from interferences caused by polyatomic ions formed from the plasma gas, entrained atmospheric gases, water, acid, and from the gallium matrix. From Table 2, it can be seen that to the light mass isotopes, their mass spectrometry were interfered so much that great attention must be paid to them. Fig.1 shows the effects of $^{40}Ar\ ^{16}O$ peak on ^{56}Fe in the high purity gallium at $m/\Delta m=8000$. The result suggests that MRM would cause a part of $^{40}Ar\ ^{16}O$ peak doubled with ^{56}Fe peak and interfered seriously, and that through HRM the interferences of $^{40}Ar^{16}O$ peak effectively disappear. Fig.2 shows the interferences of $^{40}Ar\ ^{35}Cl$ peak to ^{75}As peak at $m/\Delta m=8000$. In the HRM, ^{75}As peak was separated from $^{40}Ar\ ^{35}Cl$ peaks sufficiently. Similarly, ^{48}Ti peaks were disturbed by polyatiomic ion peaks. Therefore, these three elements were measured at

$m/\Delta m=8000$. The interference of mass spectrometry of polyatomic ions to such isotopes as ^{24}Mg, ^{106}Pd, ^{107}Ag, ^{118}Sn, ^{121}Sb and ^{208}Pb could be omitted, and the determination could go on through LRM. MRM could be used in analyzing the other 6 isotopes as ^{52}Cr, ^{55}Mn, ^{60}Ni, ^{63}Cu and ^{64}Zn.

Table 2 Isotopes of interest, mass resolution mode and some potential interference

Isotopes	Resolution mode	Main potential interferences	Detection limits/(μg/g)	Blanks/(μg/g)
^{24}Mg	LRM	Ti^{++}, Ca^{++}, BN	0.03	<0.03
^{48}Ti	HRM	SO, SN, NOO, NO_2, ArC	0.28	<0.28
^{52}Cr	MRM	ArC, ClOH, ArO, ArN, ArNH	0.05	0.19
^{55}Mn	MRM	ArO, CaO, Cd^{++}, ArN, ArNH, ClOH	0.02	<0.02
^{56}Fe	HRM	ArO, CaO, Cd^{++}	0.23	<0.23
^{60}Ni	MRM	CaO, NaCl	0.16	<0.16
^{63}Cu	MRM	TiO, ArAl, TiOH, ScO, NaAr, PO_2	0.01	<0.01
^{64}Zn	MRM	S_2, ArMg, SO_2, TiO, TiOH, Ba^{++}	0.03	<0.03
^{75}As	HRM	ArCl, CoO, ArK, NiO, CaO_2	0.04	<0.04
^{106}Pd	LRM	ZnAr, GeAr, ZrO, SrO, YO	0.01	<0.01
^{107}Ag	LRM	ZrO, ZrAr, YO	0.02	<0.02
^{118}Sn	LRM	ArSe, BrCl, RuO, MoO	0.05	<0.05
^{121}Sb	LRM	ArBr, CdNH, NbN_2	0.12	<0.12
^{208}Pb	LRM	OsO	0.03	<0.03

LRM: low resolution mode; MRM: medium resolution mode; HRM: high resolution mode

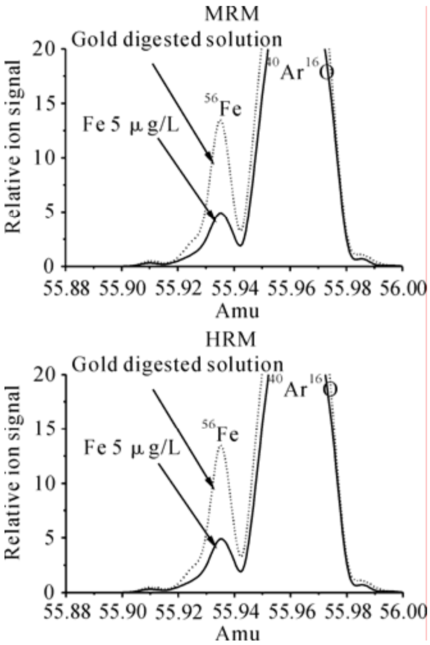

Fig.1 Mass spectra for ^{56}Fe obtained by HR-ICP-MS

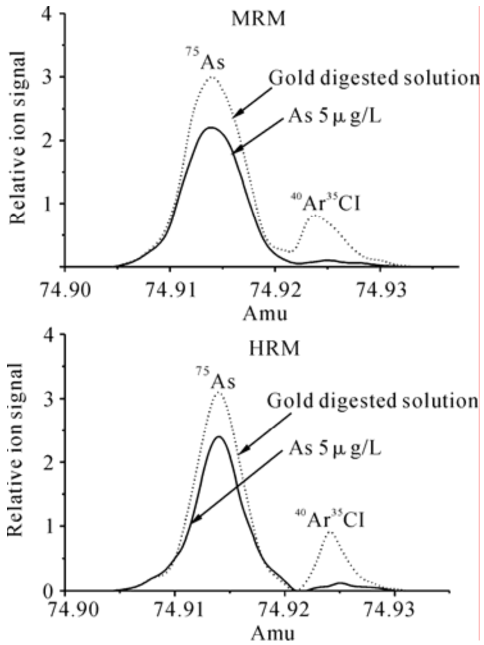

Fig.2 Mass spectra for ^{75}As obtained by HR-ICP-MS

3.2 Matrix effects

A non-spectral interference is characterized by a suppression or enhancement of the analyte signal in the presence of a matrix because of changes in sample transport, ionization in the plasma and/or ion sampling in the interface region. As is now well known, a gold matrix causes significant suppression of the analyte signal because of the high concentration of easily ionizable elements as well as signal drift caused by deposition of salt on the sampler and skimmer cones.

To assesses the effects of high gold concentrations on the determination of trace elements by ICP-MS. We measured the ion peak intensities of the analyte elements influenced by the gold matrix of several gold concentrations between 0 and 500 mg/L. HCl was used for samples decomposed. The matrix effect of Cl was negligibly small[13]. For the elements studied, it was found that the relative intensities gradually decreased with increasing gold concentration for all elements except for Mg, Cr, Fe and Ni. Internal standardization is one of the useful techniques for the correction of these interferences. A recovery test for the analyte elements together with some internal standards in a gold matrix was performed. Because it was reported that accurate correction for the matrix effect was possible using internal standard elements with mass number close to those of the analyte elements, internal standards of ^{45}Sc, ^{89}Y, ^{103}Rh, ^{115}In and ^{209}Bi were examined. These elements were frequently used as internal standard elements in ICP-MS[14, 15]. The results obtained of trace elements by ICP-QMS, after acid digestion and 10 times dilution with the addition of the internal standard elements. Found values of Mg, Ti, Mn, Cu, Zn, Pd, Sn, Sb and Pb did agree well with values for the multi-element standard solutions. However, values of Cr, Fe, Ni and As are found to be larger than those values, which are caused by the mass spectral overlapping with polyatomic ions. A significant difference in signal behavior appeared in HR-ICP-MS in comparison with ICP-QMS for the matrix tested. In this work, however, the higher resolution settings available on the HR-ICP-MS instrument resolved these elements from nearby polyatomic interferences. Fe and As were determined in the HRM. As a result, longer acquisition times were used for these elements.

The recoveries of different multi-element standards in 50 mg/mL and 100 mg/mL gold solutions were determined (Fig.3). With the exception of Cr, all analytes exhibited excellent recoveries of >90% from the sample matrix. The poor recoveries for Cr were caused by the high matrix concentration of the sample solution, which affected the chelate formation. Nevertheless, quantification of chromium in matrix-loaded sample solutions was readily possible because of the highly reproducible recovery values obtained[16].

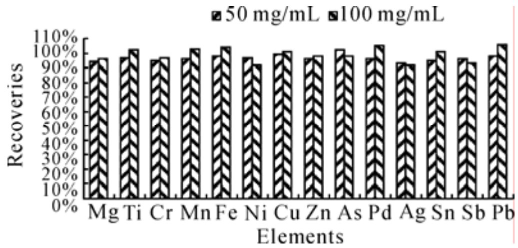

Fig.3 Recoveries of a multi-element standard (@5μg/L) from 50 mg/mL and 100 mg/mL gold solutions

3.3 Analysis of SRM 685W

In order to validate the HR-ICP-MS method, the concentrations of analyte elements were determined in the standard reference material of purity gold (NIST SRM 685W) sample. Analytical results for the SRM 685W sample together with certified values are presented in Table 3. The relative standard deviations (RSD) of 3-times duplicate analysis and the relative variances (%) are also shown in Table 3.

Table 3 shows that for analyte elements measured concentrations are in good agreement with the certified values. The RSD of the observed values were within 5%. These results indicate that the present method was precise enough to apply to the multielement analysis of the high purity gold sample.

Table 3 Analytical results for purity gold standard reference material (SRM 685W) determined by HR-ICP-MS

Element	Observed value^{a} M_{obs}/(μg/g)	RSD /%	Certified value M_{cer}	Relative variance^{b} /%
Mg	<0.03	—	<0.2	—
Ti	<0.28	—	—^{c}	—
Cr	<0.05	—	<0.05	—
Mn	<0.02	—	<0.01	—
Fe	0.31±0.02	2.2	0.3	+3.3
Ni	<0.16	—	<0.05	—
Cu	0.11±0.01	3.1	0.1	+10.0
Zn	<0.03	—	<0.04	—
As	<0.04	—	—^{c}	—
Pd	<0.01	—	—^{c}	—
Ag	0.11±0.01	1.9	0.1	10.0
Sn	<0.05	—	<0.07	—
Sb	<0.12	—	—^{c}	—
Pb	<0.03	—	—^{c}	—

a. Mean value±SD (standard deviation), n=3; b. {(M_{obs}-M_{cer})/ M_{cer}}×100, where M_{obs} and M_{cer} are observed and certified values, respectively; c. No certified value

3.4 Analytical applications

No internal standard was added to the samples. The standard addition method was employed to determine impurities in gold samples. The working curves were obtained by the addition of analyte elements to solution of sample Ⅰ and sample Ⅱ. The working curves for all the analyte elements were linear.

The detection limit was estimated as the analyte concentration corresponding to three times the standard deviation (3σ) of the blank signals obtained in the replicate measurements ($n=10$). The detection limits for analyte elements and blank tests are shown in Table 2. The detection limits obtained by HR-ICP-MS are below 0.1 μg/g for most elements. The results of blank tests for all the elements below the detection limits but Cr, it is clearly shown that the samples were treated without any significant contamination. The results for the determination of the 14 trace elements in two kinds of high purity gold samples are given in Table 4. Each result is the average of five sample determinations.

Table 4 Analytical results for commercially available high-purity gold samples/concentration (μg/g)

Element	Sample Ⅰ	Sample Ⅱ	Element	Sample Ⅰ	Sample Ⅱ
Mg	7.02±1.44	4.63±0.81	Zn	11.31±2.63	4.92±0.61
Ti	3.16±0.29	5.24±0.70	As	0.19±0.02	0.34±0.05
Cr	6.49±0.72	4.32±0.53	Pd	15.25±2.40	2.78±0.63
Mn	12.93±1.38	8.11±1.05	Ag	4.11±0.73	12.42±2.04
Fe	5.6±0.46	3.49±1.36	Sn	<0.05	6.05±1.12
Ni	0.85±0.13	0.57±0.09	Sb	<0.12	0.53±0.08
Cu	2.72±0.15	4.38±0.28	Pb	7.61±0.55	5.34±0.37

4 Conclusion

A novel and reliable method for the simultaneous determination of trace elements in high purity gold using HR-ICP-MS was established. The technique was demonstrated that HR-ICP–MS is not only a powerful diagnostic tool for determining and resolving spectroscopic interferences, but also a versatile technique for quantitative determination of analytes at low, medium, and high resolution. It was shown to be very sensitive, precise and accurate. Low detection limits and the capacity to separate analytes from potential interferences make this technique valuable for the determination of elements at the μg/g to pg/g level in high purity samples.

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