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Determination of gold by electrothermal atomic absorption spectrometry after single drop microextraction

Saeid Nazari

Department of Chemistry, Faculty of Science, Tarbiat Moallem University of Sabzevar, Sabzevar, (IRAN)

E-mail : nazari@sttu.ac.ir

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ABSTRACT

Due to the importance of gold and their extremely low levels various matrices, highly sensitive and rapid methods required for its trace and ultra trace determination. In trace element analysis, preconcentration and separation methods enhance the sensitivity and precision of the determination. In this work we describe a high sensitive method for extraction and determination of gold in aqueous samples by liquid phase microextracion combined with a graphite furnace atomic absorption spectrometry. For obtaining higher sensitivity we applied method of “single drop microextraction” for determination of trace amounts of gold. In this method Au is reacted with Orthophenylen 2-mercapto aniline, the complex formed was then extracted into micro drop of 1,2 dichloroethane. After extraction, the micro drop was retracted and directly transferred into a graphite tube modified by [$Pd_{(c)}$+$Pd_{(i)}$]. The detection limit was calculated to be 0.8μg/l (absolute value of 0.3 ng) based on $3S_b$. The relative standard deviation for five replicate analysis of 10μg/l Au was 6.5%. The calibration curve was linear in the range of 0.8 to 40μg/l with a sensitivity of 0.25μg/l.

KEYWORDS

Single drop microextraction;
Gold, 2-mercapto aniline;
Graphite furnace atomic absorption spectrophptpmetry.

INTRODUCTION

Gold is a noble metal especially resistant to heat and corrosion, and it is therefore used as a precious metal in jewelry and in some forms of chemical apparatuses. Palladium is also an excellent conductor of electricity and is used in electrical contacts and in catalytic converters. However, the concentrations of gold in environmental (also geological) materials are usually too low (even below the detection limit of the instrument) to be determined directly by conventional techniques owing to sensitivity and matrix interference. Thus, an effective preconcentration and separation procedure is usually necessary prior to determination. Gold occurs in small quantities in clays, pyrite and in almost all silver, copper, bismuth, lead, zinc, tellurium and antimony ores.

The fire assay method is the oldest and most reliable method used for the concurrent determination of gold in all gold-bearing materials. Apart from this method, other methods for the determination of silver and gold have been published. One of the known procedures is the extraction of gold with methyl isobutyl ketone (MIBK)[1-4] and its direct determination by flame atomic absorption spectrophotometry.

Graphite furnace atomic absorption spectrophotometry (GFAAS) enables the detection of low concentrations of gold, but previous extraction of the precious metals is required before their determination. In order to determine trace levels of elements an extraction and pre-concentration step is necessary. Conventionally, this can be accomplished by liquid-liquid extraction (LLE)[5]. However, LLE is time consuming, tedious, requires too much of organic solvent and can be relatively expensive. Recently solid phase extraction (SPE) has gained favour as a replacement for LLE, using low amounts of organic solvent and capability of automation[6]. Solid phase microextraction (SPME) was proposed in 1989 by Belari and Pawliszyu[7]. For SPME a small dimension fused silica fibre coated with a high temperature phase is applied, having the advantages of a higher enrichment factor, free of solvent and risk of contamination and ease of application to field sampling and automation[8]. Jeanton and Cantwell developed a newly method[9,10], “liquid phase microextraction (LPME)” which overcomes the problems of solvent evaporation (LLE, SPE) and fibre preparation in SPME. It is based on the traditional LLE technique but involves only a few microliters of organic solvent as an extractant. This method is quick, inexpensive and uses small volume of organic solvents. This technique uses simple equipment which is found in most analytical laboratories and is used for preconcentration of organic components and has been coupled with chromatography methods. In this work the LPME method is reported for determination of gold in a variety of samples. In the latter, we used headspace single drop microextraction for sequestration of arsine[11].

EXPERIMENTAL

Apparatus

A 10μl Hamilton syringe was used to suspend the drop of the acceptor phase and to inject it into the graphite furnace atomizer.

A shimadzu model AA-670 atomic absorption spectrometer with GFA-4B graphite furnace atomizer and D_2 lamp for background correction was used. Gold hollow cathode lamp (Hamamatsu photonics, Kyoto, Japan) was used as a radiation source adjusted at the operating current to the value recommended by the manufacturer. High-density graphite tubes were used as atomizer. Atomic absorption signals at 242.8 nm antimony line were recorded on a graphic printer PR-4, at peak height and gas stop mode for quantification. The measurement conditions are given in TABLE 1.

TABLE 1: Applied conditions for gold determination with GFA system

Optimum analytical conditions	
Lamp current	10 mA
Wavelength	242.8 nm
Spectral bandwidth	0.2 nm
Signal processing	peak height
Purge gas	Ar
GFA heating programme	

Stage	Furnace temperature/^{o}C	Mode	Time/s	Ar flow rate/Lmin^{-1}
Drying	150	ramp	15	1.5
Ashing	400	step	15	1.5
Atomization	2100	step	3	gas stop
Clean up	2500	step	2	1.5

Reagents

All reagents were of analytical reagent grade and triply distilled water was used throughout. Standard gold solution: Commercial solutions for AAS of 1000g/cm^3 (Merck, Darmstadt, Germany). A 2%, 2-mercapto aniline solution was prepared by dissolving 2g 2-mercapto aniline (Merck, Darmstadt, Germany) in 100 ml ethanol.

Solutions for the establishment of the calibration curve for gold were always prepared fresh on the day when recording the determination was to be performed. Modifiers of 0.1% Pd and Rh in HCl 2%, 0.1%W, 10% Ni in water were used. 0.2% 2-mercapto aniline in ethanol was used as a complexing agent.

Determination of gold via pre-concentration using “Single drop extraction” technique

10 ml of Au solution was adjusted at pH=8.5 and treated with 2ml of 0.2% 2-mercapto aniline, heated at 40^{0}C in water bath and then was transferred to a 15ml vial. After cooling to 10-15^{0}C in ice-bath it was extracted into a 4μl 1, 2 dichloroethane drop suspended on the tip of a Hamilton syringe for 15minutes. The solution was stirred (2000rpm) during the extraction (Figure 1). After the extraction was completed, the solution was directly injected into the graphite tube modified with $[Pd_{(c)}+Pd_{(i)}]$.

Tube modification

Ni modifier was used by injecting 0.2% Ni and sample solution with equal volumes. $[(W.Rh)_{(c)}+Rh_{(i)}]$ modifiers were used for coating containing 60µg of each of W and Rh from 0.1% of their solutions at temperatures of 2200^{0}C and 2000^{0}C respectively and injecting 10µl of 0.1% Rh on top of 10µl sample solution. $[Pd_{(c)}+Pd_{(i)}]$ modifier was used as coating of 60µg Pd onto the graphite tube at 1800^{0}C and injecting of 10µl solution of 0.1% Pd on top of 10µl of sample solution. $[W.Rh.Pd]_{(c)}$ modifier was used as coating of 60µg of each of W, Rh and Pd solution at the appropriate temperatures.

RESULTS AND DISCUSSION

Optimization of liquid phase microextraction

The initial object was to optimize all the parameters which could affect and control the performance of gold extraction from the aqueous samples. These include modifiers, solvent, pH, temperature, extraction time and volume of aqueous and organic phase. The effects of each parameter on the extraction process were examined and the results are as follows.

Modifiers

46 modifiers containing Pd, Ru, Rh, Ir, V, Mo, W, Ni, Mg, Ascorbic acid separately or in their combinations were tested. The results of best performing modifiers are as follows:

$[W.Rh.Pd]_{(c)}$ modifier showed the best results in contrast to $[Pd_{(c)}+Pd_{(i)}]$ for direct determination of gold. Also $[Pd_{(c)}+Pd_{(i)}]$ modifier showed the best results in determination of organic compounds of gold than $[W.Rh.Pd]_{(c)}$ modifier.

Effect of type of organic solvent

Different solvents were tested from the volatility and dissolving points of view. 1,2 dichloroethane showed the best results for extraction of gold complex(Figure 2).

pH

Gold complex solutions of different pH were tested. As can be seen from figure 3, the best pH was 8.5.

Sampling temperature

The effect of sampling temperature was studied by exposing an extraction drop for 10min in the range of 5-30^{0}C. The extraction curve showed that the amounts

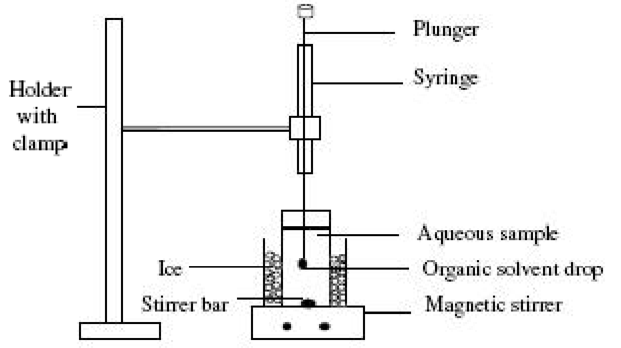

Figure 1: The schematic setup for single drop extraction

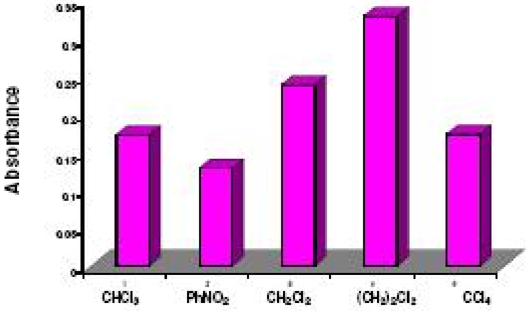

Figure 2: Effect of solvent

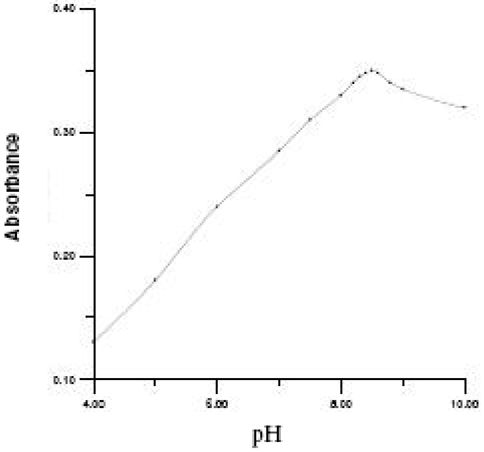

Figure 3: Effect of pH

TABLE 2: Analytical figures of merit for gold determination using different chemical modifiers

Chemical modifier	Detection[a] limit (ppb)	Sensitivity[b] (ppb)	Linear range(ppb)	RSD %[c]
$Ni_{(i)}$	8.7	3.2	8.7- 558.3	5.7
$[(W.Rh)_{(c)}+Rh_{(i)}]$	6.8	2.0	6.8 - 349.8	9.0
$[Pd_{(c)}+Pd_{(i)}]$	4.0	1.9	4.0 – 335.3	4.5
$[W.Rh.Pd]_{(c)}$	3.5	1.7	3.5 – 302.3	4.0

[a]Based on $3S_b$; [b]Calculated by dividing 0.0044 to the slope of calibration curve; [c]For 10 replicated analysis of 100µg/l Au.

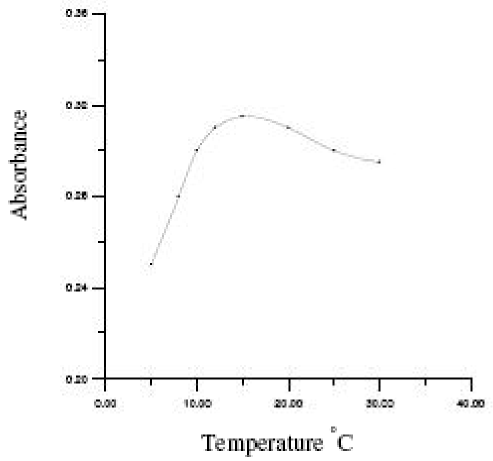

Figure 4: Effect of temperature

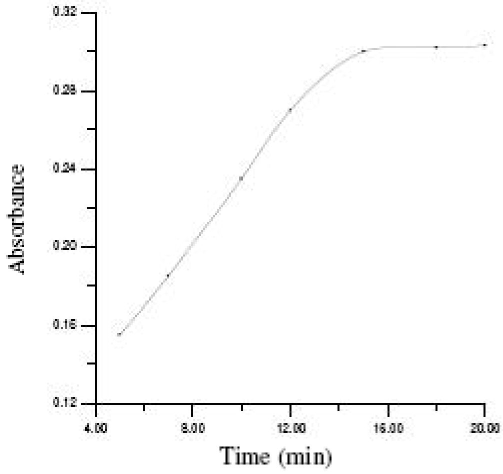

Figure 5: Effect of time

of the analyte extracted into the microdrop increased with the increase in temperature up to 15^{0}C. However temperature of 3-5 was chosen for low volatility and higher mechanical stability (Figure 4).

Extraction time

The time of extraction was varied from 5 to 30 minutes. As the results show (Figure 5) the optimum time of extraction is 25 minutes.

Volume of aqueous and organic phase

Changing the organic volume from 1to 4μl increased the extraction efficiency. However higher volumes were avoided due to mechanical instability. 10ml solution volume was chosen for the analysis as lower volumes caused falling of the drop due to agitation and higher volumes showed no benefit for the extraction process and were not used.

TABLE 3: Effect of interferences on determination of 4μg/l gold in the presence of 100 fold of foreign ions

Ion	Relative absorbance[a]	Ion	Relative absorbance
Ag(I)	1.10	Pb(II)	1.00
Al(III)	1.00	Sb(III)	0.96
Ba(II)	1.00	Se(IV)	1.00
Bi(III)	1.00	Sn(II)	0.95
Ca(II)	1.00	Sr(II)	1.00
Cd(II)	1.2	Zn(II)	1.00
Co(III)	1.00	Br^-	1.00
Cu(II)	0.95	Cl^-	0.85
Fe(III)	1.00	F^-	1.05
Ge(IV)	0.94	NO_3^-	0.95
K(I)	1.00	PO_4^{3-}	1.00
Hg(II)	0.90	I^-	1.00
Na(I)	1.00	SO_4^{2-}	1.00

[a] The relative absorbance is defined as: Relative absorbance = (Absorbance of 4μg/l gold + foreign ion 400μg/l)/Absorbance of 4μg/l gold. All results are the average of triplicate measurements

TABLE 4: Results (mean ± standard deviation based on five replicate analysis) of determination of gold in SRM

SRM	Reported value	Measured value	Recovery(%)
JR-1[1]	16.3μg/g	16.8 ± 1.6μg/g	103
JG-1a[1]	0.43μg/g	0.45± 0.05μg/g	105
1643d[2]	56.02±0.73μg/l	54.05±4.85μg/l	96

[1] Obtained from geological survey of Japan, GSJ; [2] From National Institute of Standard and Technology NIST (USA).

Effect of interferences

Interfering species at 100 fold excess were added to the Au solution and the extraction was followed. The following TABLE shows the results:

The severe interferences were due to Cd^{2+}, Ge^{4+}, Sb^{3+}, Sn^{2+}, $Cd^{2+}$and Hg^{2+}.

Analytical figures of merit

Calibration curve was calculated based on 10ml of aqueous solution of gold treated at the optimized conditions. The calibration curve was linear in the range of 0.5μg/l to 40μg/l gold with a correlation coefficient of 0.9936 and the atomic absorption sensitivity was 0.25μg/l. The detection limit was calculated to be 0.8μg/l based on $3S_b$. The relative standard deviation (RSD) for five replicate analysis of 10μg/l gold was 6.5%.

Application

In order to evaluate the accuracy and recovery of the proposed method, standard reference materials SRM 1643d from NIST (USA), JG-1a and JR-1 obtained from the geological survey of Japan were analysed for their gold contents. The quantitative results given in TABLE 4 show that the method is accurate and reliable and could be applied for determination of gold in real samples.

CONCLUSIONS

The results show a very promising technique for determination of gold in a variety of samples at μg/l levels without the needs for any sophisticated device. Apart from having extremely high sensitivity, the procedure is very simple, nearly fast and benefits a very low detection limit. By the use a preliminary separation step using a resin, the method could be relatively free from interferences. The experimental parameter such as chemical modifier, organic solvent, pH of aqueous phase, sampling temperature, extraction time and volume of aqueous and organic phase have great effects on the sensitivity of method and should be optimized. The results show that gold could be determined with very high sensitivity and relatively good reproducibility in aqueous samples.

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