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Ultrasound-Assisted Emulsification Dispersive Liquid-Liquid Microextraction Based on Solidification of Floating Organic Droplet for Separation of Trace Gold Prior to Flame Atomic Absorption Spectroscopy Determination

Sayed Zia Mohammadi[1,2], Mohammad Ali Karimi[1,3], Ali Shiebani[4], Laleh Karimzadeh[2]
[1]*Payame Noor University, Tehran, Iran*
[2]*Department of Chemistry, Payame Noor University, Kerman, Iran*
[3]*Department of Chemistry & Nanoscience and Nanotechnology Research Laboratory (NNRL), Faculty of Sciences, Payame Noor University, Sirjan, Iran*
[4]*Department of Chemistry, Islamic Azad University, Yazd Branch, Yazd, Iran*
E-mail: szmohammadi@yahoo.com

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Abstract

In the present work, a ultrasound-assisted emulsification dispersive liquid-liquid microextraction based on solidification of floating organic droplet method has been developed as a sample preparation method prior to flame atomic absorption spectrometry determination of trace amounts of gold in the standard, wastewater and river water samples. In the proposed method, 1-dodecanol and 5-(4-dimethylamino-benzylidene) were used as extraction solvent and chelating agent, respectively. Several factors that may be affected on the extraction process, such as type and volume of the extraction solvent, ionic strength, pH of the aqueous solution, extraction temperature and extraction time were studied and optimized. Under the best experimental conditions, the calibration curve exhibited linearity over the range of 8.0 ng·mL^{-1}- 3.0 µg·mL^{-1} with a correlation coefficient of 0.9978 and detection limit based on three times the standard deviation of the blank signal was 1.5 ng·mL^{-1}. Eight replicate determinations of 0.2 and 1.0 µg·mL^{-1} of gold gave a mean absorbance of 0.051 and 0.253 with relative standard deviations of ±2.3% and ±1.5%, respectively. Finally, the developed method was successfully applied to the extraction and determination of gold ions in a silica ore, wastewater, river water and standard samples and satisfactory results were obtained.

Keywords: Ultrasound-Assisted Emulsification, Microextraction, Solidification, Floating Organic Droplet, Preconcentration, Gold Determination, Silica Ore

1. Introduction

Gold belongs to the group of elements which occur on the Earth in very low natural contents. The concentration of gold in the natural waters is extremely low and is in the range of 0.05 - 0.2 ng·mL^{-1} in seawater and river water, respectively [1]. It is well known that gold is one of the most interesting micro amount elements due to its significant role on biology, environment and industry. It could be used as a drug in the supervised therapy of arthritis and cancer [2] in the forms of different Au(I) and Au(III) compounds, or in radiotherapy of cancer in the form of radioactive isotope ^{198}Au. Also, it could be very toxic for human, animal and plants and account as a pollutant, because of its inhibiting effect upon the activity of many enzymes and its preventing effect upon the DNA separation [2]. Numerous methods such as, spectrometric methods [1], UV-Vis spectrophotometry [2,3], electrothermal atomic absorption spectrometry [4], inductively coupled plasma combined with optical emission spectrometry [5,6] or mass spectrometry [7] and flame atomic absorption spectrometry (FAAS) have been proposed for the determination of gold in different environmental samples. However, most of aforementioned methods except to FAAS involve a greater cost and increased instrumentation complexity, limiting its widespread application to routine analytical works. FAAS is still being used because it combines a fast analysis time, a relative simplicity and a cheaper cost. All of these features have been responsible for its broad utilization in the determination of trace elements in different samples [8-10]. However, trace level determination of gold by FAAS is difficult due to lower levels of gold than detection limit of FAAS and effects of the matrix components [9]. To overcome these limitations on the determination of gold by FAAS, separation-enrichment techniques including solid phase extraction (SPE), cloud point extraction, liquid–liquid extraction (LLE), coprecipitation, etc. [11-17] have been used by the researchers around the world.

For many decades, the most common methods for the performing of the analytical separation were LLE. LLE is time-consuming and needs to large amounts of toxic organic solvents. These shortcomings have led to the development of the new cost-effective methods with special emphasis on resolving the mentioned difficulties and detecting analytes at very low concentrations. Recently, efforts have been directed towards miniaturization of the LLE procedure by reducing of the amount of organic solvent and leading to the development of liquid-phase microextraction methods. Liquid-phase microextraction (LPME) was introduced by Jeannot and Cantwell in 1996 [18], however, the major disadvantage of LPME is time-consuming**.** Efforts to overcome of this particular limitation led to the development of dispersive liquid–liquid microextraction (DLLME) method [19]. In this method, an appropriate mixture of extraction and disperser solvent are used. The surface area between the extraction solvent and sample solution are infinitely large because a cloudy solution can be formed. Therefore, the extraction equilibrium can reach quickly. The method has attracted much attention due to their advantages such as fast analysis, low consumption of organic solvent and simplicity [20,21]. However, the extraction solvent is limited in solvents, which should have higher density than water, such as chlorobenzene, chloroform, tetrachloromethane and carbon disulfide, and all of them are toxic and environment-unfriendly.

The application of ultrasounic-assisted radiation in the LLE methods (USALLE) has been reported by Luque de Castro and Priego-Capote [22,23]. They also successfully applied ultrasound-assisted emulsification (USAE) for the first time to determine some polar and non-polar compounds in solid plant samples [24]. High extraction efficiency in a short period of time is the main advantage of the USALLE. Regueiro et al. applied a miniaturized approach to USALLE by using a micro volume of organic phase to provide the advantage of both DLLME and USALLE [25]. They successfully applied ultrasound-assisted emulsification microextraction (USAEME) to determination of some emergent contaminants and pesticides in environmental waters. Fontana et al. applied this method for determination of polybrominated flame retardants in water samples [26]. They demonstrated that USAEME is an efficient, simple, and rapid as well as cheap extraction technique prior to the GC analysis.

Recently, a new mode of liquid-phase microextraction based on solidification of floating organic droplet (LPME-SFO) was developed [27,28]. In this method, no specific holder, such as the needle tip of micro syringe, the hollow fiber and polychloroprene rubber tube, is required for supporting the organic micro drop due to the using of organic solvent with low density and proper melting point. Furthermore, the extractant droplet can be collected easily by solidifying it in the lower temperature. However, the extraction time was somewhat long, thus it cannot satisfy the demand of fast analysis.

Recently, Xu and co-workers in 2009 [29] combined the advantages of the two methods (DLLME and LLME-SFO) and develop a new method named dispersive liquid–liquid microextraction based on solidification of floating organic droplet (DLLME-SFO). In this method, the enormous contact area between the organic droplets and sample solution is beneficial for the fast mass transfer from the aqueous phase to the organic phase. Accordingly the analysis time is shortened greatly. Moreover, the transfer of the solidified phase from aqueous phase can be carried out easily.

Pourreza [30] and Afzali [31] reported that 5-4-dimethylamino-benzylidene (rhodanine) is suitable as a sensitive and selective reagent for gold. Therefore, rhodanine was selected as chelating agent in the present work.

The aim of this work is combination of USAEME with SFO and developing a new method as name USAEME-SFO for the determination of trace gold in river water and wastewater samples. All main factors were investigated and optimized. The USAEME-SFO method was evaluated by analyzing Certified Reference Materials and spiked samples.

2. Experimental

2.1. Instrumentation

A SensAA GBC (Dandenong, Australia) atomic absorption spectrometer equipped with deuterium background correction and gold hollow cathode lamp was used for absorbance measurements at wavelength of 242.8 nm. The instrumental parameters were adjusted according to the manufacturer's recommendations. Acetylene flow rate and burner height were adjusted in order to obtain the maximum absorbance signal, while aspirating the analyte solution. A Metrohm 692 pH meter (Herisau, Switzerland) was used for pH measurements. An ultrasonic bath with temperature control (FALC instruments S.V.l Treviglio, Italy) model LBS2 was used to assist the emulsification process of the microextraction technique.

2.2. Reagents and Solutions

All chemicals were analytical-reagent grade (Merck, Darmstadt, Germany) and were used without previous purification. The laboratory glassware was kept overnight in a 1.4 mol·L^{-1} HNO_3 solution. Before using, the glassware was washed with de-ionized water and dried. Stock solution of gold at a concentration of 1000.0 µg·mL^{-1} was prepared by dissolving an appropriate amount of $HAuCl_4 \cdot 3H_2O$ (Merck) in double distilled water. The working reference solutions were obtained daily by stepwise dilution from stock solution. A 0.05% (w/v) solution of 5-(4-dimethylamino-benzylidene) (Rhodanine) (Mer- ck) was prepared by dissolving it in ethanol. The solutions of alkali metal salt (1% w/v) and various metal salts (0.1% w/v) were used to study the interference of anions and cations, respectively.

2.3. USAMEM-SFO Procedure

All standards and samples were prepared for analysis according to the following procedure. Eight mL of each sample was placed in a screw cap glass test tube. To each test tube, 1 mL of 0.1 mol·L^{-1} phosphate buffer (pH 3), 100 µL Rhodanine 0.05% in ethanol and 1 mL of 10% (w/v) NaCl were added. Then, 25.0 µL 1-dodecanol was injected into each solution and all samples were sonicated for 10 minutes at 42˚C in ultrasonic bath. As a result, oil-in-water emulsions of 1-dodecanol in water were formed. After centrifuging at 4000 rpm for 4 min, the organic solvent droplet was floated on the surface of the aqueous solution due to low density below water. Then, the sample vial was put into an ice bath for 5 min, at this time the floated solvent was solidified because of low melting point (24˚C). Then, the solidified solvent was transferred to a conical test tube. The extractant in the test tube was washed by iced water for 2 times, and the water in the vial was drawn out by a syringe. The solidified organic solvent melted quickly at room temperature. Prior to analysis of gold by FAAS, the extractant was mixed with 0.5 mL of dimethyleformamid.

2.4. Sample Preparation

In order to test the reliability of the proposed USAMEM-SFO procedure for extraction and determination of gold in the real samples, two Canadian Certified Reference Materials Project (CCRMP) and a silica ore sample (Muteh gold mine, Isfahan, Iran) were analyzed. For this purpose, 200.0 mg of CCRMPs and 1.00 g of silica ore sample were taken and dissolved completely in a mixture of nitric acid, hydrochloric acid and HF (2:6:1) with heating. The solutions were cooled, diluted and filtered. Then, the filtrates were made to 50.0 mL with deionized water in a volumetric flask.

River water and wastewater samples were collected in acid leached polyethylene bottles. River water sample was collected from Shahdad (Kerman, Iran) and wastewater samples were collected from copper factory in Sarcheshmeh area (Kerman, Iran) and Bahonar copper factory in Kerman. The only pretreatment was acidification to pH 2 with nitric acid, which was performed immediately after collection, in order to prevent adsorption of the metal ions on the flask walls. The samples were filtered before analyses through a cellulose membrane (Millipore, Bedford, MA, USA).

3. Results and Discussion

3.1. Type and Volume of the Extraction Solvent

Selection of the extraction solvent is important in the optimization of USAEME-SFO conditions. It should have low solubility in water, high affinity to analytes, lower melting point than room temperature and lower density than water. In this work, 1-undecanol and 1-dodecanol were selected as extraction solvent, and their extraction efficiency were studied. The results were shown that both of solvent are suitable for extraction of gold. 1-undecanol is more expensive than 1-dodecanol (DOD), therefore DOD was selected as the extraction solvent in the subsequent experiments. The effect of the DOD volume on the extraction efficiency was also investigated. Therefore, some experiments were performed with different volumes of DOD (15.0 - 50.0 µL) as the extraction solvent and keeping the other variable constant. The results are shown in **Figure 1**. It was observed that the maximum extraction efficiency was obtained at the volume range of 20.0 to 50.0 µL of DOD. Thereby, 25.0 µL DOD was used as extraction solvent in the subsequent experiments.

3.2. Effect of pH on the USAEME-SFO Procedure

The pH plays a unique role on the metal-chelate formation and the subsequent extraction. Therefore, the effect of pH on the USAEME-SFO extraction of gold was studied in

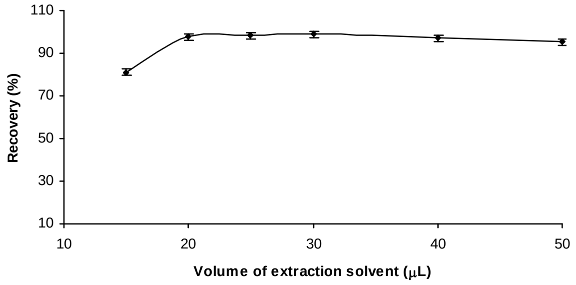

Figure 1. Effect of the extraction solvent volume (DOD) on the USAEME-SFO extraction of gold. Conditions: Au(III), 8.0 μg; Buffer with pH 3, 1 mL; NaCl 1% (w/v); Extraction time, 10 min; Extraction temperature, 42˚C.

the pH range of 1 - 9 and keeping the other variable constant. The results are shown in **Figure 2**. As can be seen in **Figure 2**, the highest extraction efficiency of gold was obtained at the pH range of 2.5 - 3.5. Therefore, pH 3 was selected for the further experiments.

3.3. Effect of the Extraction Temperature

Temperature affects organic solvent solubility in water as well as the emulsification phenomenon. Thus, this affects the mass-transfer process and the extraction efficiency. To determine the influence of the extraction temperature, 8.0 mL aqueous solution containing 8.0 μg of gold was extracted at different temperatures ranging from 30˚C to 60˚C. The results are shown in **Figure 3**. It was observed that the highest extraction efficiency was obtained at the range of 40˚C - 45˚C. Hence, 42˚C was used for further experiments.

3.4. Effect of the Extraction Time

In USAEME, the extraction time is defined as interval time between the injection of the extraction solvent and the starting of centrifuge. Effect of the extraction time was examined in the range of 5 to 20 min and keeping the other variable constant. The results are shown in **Figure 4**. It was observed that the highest extraction efficiency was obtained at 7.5 - 12.5 min. Based on these observations; an extraction time of 10 min was used for further experiments.

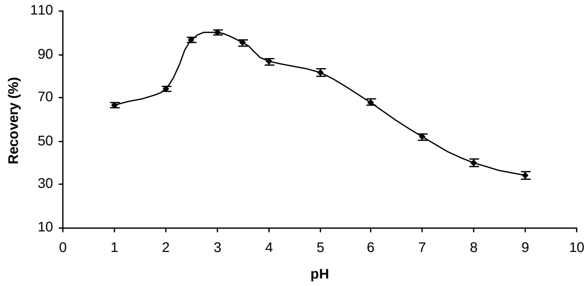

Figure 2. Effect the pH of sample solution on the USAEME-SFO extraction of gold. Conditions were the same as Figure 1 except to pH.

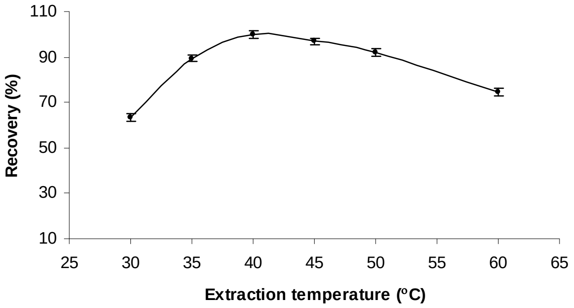

Figure 3. Effect of the extraction temperature on the USAEME-SFO extraction of gold. Conditions were the same as Figure 1 except to extraction temperature.

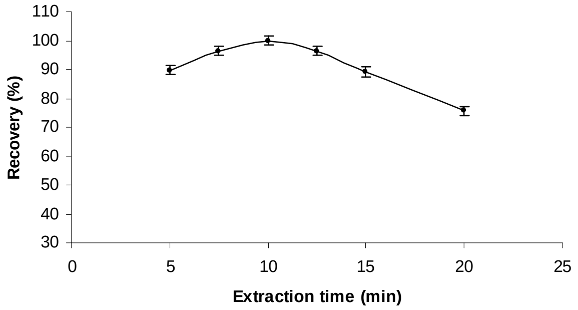

Figure 4. Effect of the extraction time on the USAEME-SFO extraction of gold. Conditions were the same as Figure 1 except to extraction time.

3.5. Effect of Ionic Strength

In the extraction methods, the solubility of many analytes in aqueous solutions decreases with increasing ionic strength due to salting out effect. For investigating the influence of the effect ionic strength on the USAEME-SFO extraction of Au(III) ion, sodium chloride solution was used in the concentration range of 0.25% to 2.5% (w/v). The results were shown that the highest recovery percent of gold ion was obtained at 0.75% - 1.25% NaCl concentration. Below or above this concentration range, a decrease on the extraction efficiency was observed. Therefore, 1% NaCl concentration was used in the subsequent experiments.

3.6. Interference

The efficiency of the USAEME-SFO procedure in the extraction and preconcentration of gold ions were also studied in the presence of various cations and anions. In order to, interference ions in different interference-to-analyte ratios were added to a solution containing 8.0 μg of Au(III) and were subjected to the USAEME-SFO procedure. The tolerance limit was set as the amount of ion required to cause ±5% error in the determination of gold. The results are given in **Table 1**. The results were shown that the presence of large amounts of species commonly present in water samples have no significant effect on the extraction of gold.

3.7. Analytical Figures of Merit

Figures of merit of the USAEME-SFO procedure were obtained by processing of the standard solution of gold. For a sample volume of 8 mL, the calibration graph exhibited linearity over the range of 8.0 ng·mL^{-1} - 3.0 μg·mL^{-1} with a correlation coefficient of 0.9978 ($A= 0.2549C + 0.0026$, where A is the absorbance value and C is the concentration of gold (μg·mL^{-1}). The relative standard deviations ($n = 8$) at 0.2 and 1.0 μg·L^{-1} of gold were ±2.3% and ±1.5%, respectively. The limit of detection, based on three times the standard deviation of the blank signal was 1.5 ng·mL^{-1} of gold. The enrichment factor was calculated as the ratio of the analytical signal of Au obtained after and before extraction. The enrichment factor was 14.2 for 8.0 mL sample solution.

Table 1. Tolerance limit of interference ions.

Interference ions	Interference/gold ratio	Recovery (%)
PO_4^{3-}, $H_2PO_4^-$, HPO_4^{2-}	>5000	95
K^+	3000	104
Na^+	3500	105
Ca^{2+}	3000	95
Mg^{2+}	2500	105
Co^{2+}	700	95
Mn^{2+}	500	105
Ni^{2+}	600	98
Cu^{2+}	400	105
Pb^{2+}	500	95
Cd^{2+}	600	96
Pd^{2+}	600	104
Rh^{3+}	800	105
Zn^{2+}	300	95
Ag^+	200	95
Fe^{3+}	100	96
Al^{3+}	50	95

Conditions were the same as **Figure 1**.

3.8. Accuracy of the Method

The accuracy of the USAEME-SFO procedure was checked to the determination of gold in CCRMP (MA-1b and CCU-1b). An aliquot of the sample solution was taken and gold was determined after the USAEME-SFO procedure. The results are given in **Table 2** and are in good agreement with the certified value.

3.9. Application

The USAEME-SFO procedure was applied to the determination of gold in a silica ore, wastewater and river water samples. The recovery of gold from the silica ore, wastewater and river water samples spiked with the known amounts of gold ions was also studied. The obtained results are shown in **Table 3**. According to these results the added gold ions spiked to the wastewater and river water samples can be quantitatively recovered, and no significant interference was observed.

Furthermore, the ore sample was analysed by inductively coupled mass spectrometry (ICP-MS) technique for verifying the result obtained by the USAEME-SFO procedure developed in this paper. As it is obvious from

Table 2. Determination of gold in canadian certified reference materials project.

Sample	Certified value (μg g^{-1})	Found[a] (μg g^{-1})
MA-1b reference gold ore	17.0	17.1 ± 0.5
CCU-1b copper flottation concentrate	5.89 ± 0.10	5.86 ± 0.17

[a]Average±standard deviation (n = 4).

Table 3. Determination of gold in real samples.

Sample	Gold amount (ng·mL^{-1}) Added	Gold amount (ng·mL^{-1}) Found[a]	Recovery (%)
Silica ore (Muteh gold mine, Isfahan, Iran)	0.0	41.40 ± 1.80[b]	-
	10.0	51.23 ± 0.5	98.3
Shoor river (Shahdad, Kerman)	0.0	N.D.[c]	-
	10.0	9.8 ± 0.3	98.0
Wastewater (copper factory, Sarchashmeh, Rafsanjan)	0.0	B.L.R.[d]	-
	10.0	10.6 ± 0.4	106.0
Wastewater (copper factory, Shahid Bahonar, Kerman)	0.0	B.L.R.	-
	10.0	10.4 ± 0.4	104.0

[a]Mean ± standard deviation (n = 4). [b]The quantitative analysis of gold content in the silica ore sample by the proposed method and ICP-MS was found to be 2.07 ± 0.09 μg g^{-1} and 2.11 ± 0.12 μg·g^{-1}, respectively. [c]Not detect. [d]Below of linear range.

Table 3, there is a satisfactory agreement between the results obtained by ICP-MS (2.11 ± 0.12 $\mu g \cdot g^{-1}$) and the proposed method (2.07 ± 0.09 $\mu g \cdot g^{-1}$).

4. Conclusions

In this paper, we introduced a USAEME-SFO method for the analysis of trace amounts of gold in wastewater and river water samples. The USAEME-SFO procedure has numerous advantages such as: low cost, low toxic, simplicity of operation, rapidity and high selectivity. In addition, it is important to point out that USAEME-SFO is a low organic solvent consuming extraction technique, which turns it into a low cost and also an environmentally friendly technique. In this method, the consumption of the toxic organic solvent (at microlitre level) was minimized without affecting sensitivity of the method.

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