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Supramolecular solvent microextraction of gold prior to its determination by microsample injection system coupled with flame atomic absorption spectrometry *

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Abstract

A supramolecular solvent based liquid-liquid microextraction (SsLLME) system for gold was developed prior to its microsample injection system coupled with flame atomic absorption spectrometric (MS-FAAS) determination. 1,3,4-thiadiazole-2,5-dithiol was used as complexing agent to obtain hydrophobic complex. The analytical factors affecting the microextraction efficiency, such as pH, type and volume of supramolecular solvent, amount of complexing agent, ultrasonication and centrifuge time and sample volume were investigated. The limit of detection (LOD), enhancement factor (EF) and relative standard deviation (RSD) of the method was 1.5 μg L^{-1}, 51 and 4.2 %, respectively. The accuracy of method was checked by analysis of CDN-GS-3D Gold Ore certified reference material and addition-recovery tests. The method was successfully applied for the determination of gold in environmental samples.

Keywords: Supramolecular solvent, Microextraction, Gold, Flame atomic absorption spectrometry.

*This study is a part of PhD thesis of Erkan Yilmaz

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1. Introduction

Gold is the most important noble metal, due to its usage in jewelry, pharmaceutical application and industry, etc.[1-4] Concentrations of gold in real samples like environmental and pharmaceutical materials are usually below the detection limit of the flame atomic absorption spectrometer to be determined directly, due to insufficient sensitivity and effects of the matrix interference.[1, 5, 6] Hence, under these circumstances, a simple, sensitive and selective separation and preconcentration procedure method for determination of trace gold in real samples were required prior to flame atomic absorption spectrometric determination.[1, 2, 5-7] Various separation and enrichment methods such as including solid phase extraction (SPE),[1, 8] cloud point extraction,[9, 10] liquid–liquid extraction,[11] coprecipitation, etc.[12] have been developed by the scientists. However these methods have some disadvantages like high consumption of toxic organic solvents and generate secondary toxic waste, difficult and tedious operation and time consuming.[13-17] In order to eliminate these disadvantages, small-scale preconcentration-separation methods called microextraction including dispersive liquid-liquid microextraction,[13, 14] hollow fiber liquid phase microextraction,[18] solid phase microextraction[17] and ultrasound-assisted emulsification of solidified floating organic drop microextraction[19] have been developed for preconcentration and separation of gold from various media.

A new mode of microextraction technique named supramolecular solvent based liquid-liquid microextraction (SsLLME) has been developed for preconcentration and separation of organic and inorganic species.[20-24] Supramolecular solvents (Ss) are obtained from amphiphile solutions by two well-defined self-assembly global processes. The processes occur on two scales, nano and molecular by the external effects like pH, temperature and electrolyte concentration of sample, type and volume of solvent. First, amphiphiles aggregate to obtain supramolecular assemblies, like reverse micelles or vesicles or aqueous, in a homogenous solution and then, coacervate in a second step and give water-immiscible phase that separate from the bulk solution.[20-24] In microextraction studies, the interactions between analytes in water phase and extraction phase are important to increase extraction efficiency.[21, 25] Hence, the selection of suitable extraction medium is important step. The supramolecular solvents have a lot of interaction area such as hydrophobic, dispersion forces and hydrogen bonding for organic analytes and metal-ligand complex.[20-24] The interaction areas in supramolecular assemblies provide high extraction capability and short extraction time. The preparation of supramolecular solvents at room temperature using conventional, cheap and harmless chemicals is the most important advantage.[20-24] The supramolecular solvent used was formed reverse micelles of 1-Decanol in the nano- and microscale regimes dispersed in a continuous phase of tetrahydrofuran (THF): water. The basis of supramolecular solvent based microextraction method is hydrophobic and π-cation interactions and the formation of hydrogen bonds between analyte and supramolecular solvent phase. The hydrophobic character and water immiscibility of certain supramolecular solvents allow their use in solvent extraction of hydrophobic compounds.

In the present study, the supramolecular solvent based liquid-liquid microextraction method (SsLLME) for the preconcentration and separation of gold in environmental samples was developed prior to its microsample injection-flame atomic absorption spectrometric determination.

2. Experimental

2.1. Chemicals and solutions

All solutions were prepared with reverse osmosis purified water (18.2 MΩ cm, Millipore). Except if otherwise stated all chemicals used were analytical reagent grade and were used without further purification. Extraction solvents (1-Decanol, Undecanol) and THF were purchased from Merck (Darmstadt, Germany). Decanoic acid was purchased from Sigma-Aldrich (St. Louis, MO, USA). Concentrated (36 % (v/v)) HCl (Merck, Darmstadt, Germany) and 65% HNO_3 (E. Merck, Darmstadt, Germany) were used.

The model solutions of gold(III) was established using standard solutions prepared by dilution from 1000 mg L^{-1} gold(III) stock solution (E. Merck, Darmstadt, Germany). Gold Ore CDN-GS-3D certified reference material (CDN Resource Laboratories Ltd. Canada) was also used. A solution of 0.1% (m/v) of 1,3,4-thiadiazole-2,5-dithiol (Aldrich, USA) was daily prepared in ethanol. In order to adjust of pH of sample solutions, Buffer solutions were prepared by using combination of salts and solutions as follows: phosphate buffer solution (pH 2.0–4.0, sodium dihydrogen phosphate/phosphoric acid), acetate buffer solution (pH 5.0-6.0 ammonium acetate/acetic acid), phosphate buffer solution (pH 7.0-7.5 sodium dihydrogen phosphate/disodium hydrogen phosphate).

2.2. Instrumental

A Perkin-Elmer Model 3110 flame atomic absorption spectrometer (Norwalk, CT, USA) including a gold hollow cathode lamp (operated conditions as follows: wavelength 242.8 nm, spectral band width: 0.7 nm and lamp current: 15.0 mA). Air–acetylene flame was used for absorbance measurements. The continuous aspiration mode was used for determination of extracted gold concentration in last volume. The samples were introduced into the nebulizer of the FAAS by using a home made micro-injection unit including Teflon funnel which connected to the nebulizer with capillary tubing.[25, 26] 100 µl of the samples was injected to the micro-injection unit by using Eppendorf pipette and peak heights were measured as signals. In order to produce supramolecular solvent, an ultrasonic water bath (Norwalk, CT, USA) was used. A Sartorius PT-10 model pH meter with glass-electrode was used for pH adjustments of sample solutions (Sartorius Co., Goettingen, Germany). The centrifugation was performed using an ALC PK 120 model centrifuge (Buckinghamshire, England).

2.3. Supramolecular solvent based liquid–liquid microextraction procedure

A graphical diagram of the SLSDE-ILDLLME protocol was shown in Fig. 1. A 10 mL of sample solution containing 0.5 µg Au(III), 0.05 mg 1,3,4-thiadiazole-2,5-dithiol and 2 mL of pH 6 buffer solution were placed into a 50-mL polypropylene centrifuge tube. Then, the extraction solution, which prepared by mixing 50 µL 1-decanol and 200 µL THF, was injected in to the sample solution and the tube was capped. The mixture was kept in an ultrasonic bath for 3 min and the supramolecular solvent, made up 1-Decanol dispersed in THF: water spontaneously formed. The obtained mixture was centrifuged at 4000 rpm for 3 min to accelerate the complete separation of the water and extraction phase. The supramolecular solvent phase situated at the top of the water phase because of its lower density than water, was taken by using micropipette and its volume completed to 250 µl with ethanol.

(Fig 1. here)

2.4. Analysis of real samples

The supramolecular solvent based liquid–liquid microextraction procedure was applied to gold ore samples and rock samples obtained from different cities of Turkey (Ordu, Samsun, Nigde and Erzincan) Turkey. The ore and rock samples were homogenized with an agate homogenizer and dried at 80 ^{o}C for 24 hour.

Ore (0.1 g) and rock samples and 0.15 g of certified reference material CDN-GS-3D Gold Ore was weighed, placed into a 100-mL beaker, and digested with 30 mL of aqua regia at 95 °C until semidried masses were obtained. The resulting mixture again was mixed with 30 mL of aqua regia and evaporated almost to dryness. 5 mL of purified water was added to the residue. The suspension was filtered through a blue band filter paper (Macherey-Nagel, Düren, Germany), and the insoluble part was washed with purified water. Then, the SsLLME procedure given in section 2.3 was applied to the samples.

The suggested method was applied to tap from Canakkale and well water from Sivas, Turkey. The water samples were filtered through a Millipore® cellulose membrane filter (0.45 μm pore size) and the suggested SsLLME procedure (Section 2.3) was applied to the 7.0 mL of water samples.

3. Results and discussion

In order to obtain quantitative recoveries of gold(III), the microextraction procedure was optimized for various analytical parameters. The conditions for preconcentration of gold ions were selected using model solutions.

3.1. Influence of pH

pH of the working media is most critical parameter on the supramolecular solvent based liquid phase microextraction studies to obtain the supramolecular solvent and subsequent extraction of metal–ligand complex.[27] The effect of pH of the sample solution on the extraction efficiency of gold(III) were investigated in the pH range 2.0–7.5. The results given in Fig. 2 reveal that the best recovery can be achieved when the pH of sample solution was adjusted at 6.0. It is because of the neutral character of Au(III)-1,3,4-thiadiazole-2,5-

dithiol complex in this interval and the type of interactions governing its solubilisation in the supramolecular solvent phase. Therefore, pH 6.0 as working pH was chosen for the subsequent experiments.

(Fig 2. here)

3.2. Type of supramolecular solvent

The high extraction capability of the supramolecular solvent was consequence of both the power of analyte–extractant interactions and the special structure of the aggregates making it up.[21, 28] To obtain the best supramolecular solvent phase, three supramolecular solvent including decanoic acid-THF, 1-decanol–THF and undecanol- THF were used in this study. The recovery % values of gold (III) by using 1-decanol-THF, undecanol-THF and decanoic acid-THF were 100±2, 53±0 and 63±6, respectively. 1-decanol-THF supramolecular solvent was used as extraction phase for the further study.

3.3. Influence of the volume ratio of 1-decanol and THF

The effect of the 1-decanol/THF volume ratio on the recovery of gold was also studied. To study the effect of varying the volume of supramolecular solvent on the efficiency of the extraction of gold from sample solution, the volume of 1-decanol was changed between 50 and 300 µL and the THF was kept constant at 600 µL. Fifty µL volume of 1–decanol was adequate for quantitative recovery of gold. The effect of the volume of THF on the extraction recovery was also studied. Different volumes of THF in the range of 100–600 µL with addition of 50 µL of 1-Decanol were examined. The results illustrated in Fig. 3 reveal that after 200 µL, the recoveries stayed quantitative and consequently, 200 µL of THF was selected as the optimum volume.

(Fig 3. here)

3.4. Effect of complexing agent amount

The extraction efficiency depends on the hydrophobicity of the complexing agent which provides solubility of metal complex in supramolecular solvent phase.[21] For this purpose, 1,3,4-thiadiazole-2,5-dithiol was used as complexing agent because of the highly hydrophobic nature of its gold complex. Amount of complexing agent has a critical effect on the quantitative recoveries of the analytes in liquid phase microextraction.[29] Thus, it is highly important to establish the minimal complexing agent amount that leads to total complex formation while getting the highest recovery. The effect of amount of 3,4-thiadiazole-2,5-dithiol was also investigated in the range of 0.0-0.5 mg. The results are depicted in Fig. 4. A amount of 0.05 mg of 3,4-thiadiazole-2,5-dithiol was selected for the further experiments.

(Fig 4. here)

3.5. Effect of ultrasonication and centrifuge time

It is known that ultrasonic radiation is an important way to increase the kinetics and extraction efficiency. The ultrasonic radiation increases the interactions between analyte in sample solution and extraction phase for mass transfer.[30, 31] In this study, an ultrasonic water bath was used for formation of supramolecular solvent made up of reverse micelles of 1-decanol dispersed in THF: water and extraction of Au(III)-1,3,4-thiadiazole-2,5-dithiol complex. The effect of ultrasonication time on extraction efficiency was examined in the range of 2–4 minute. Three minute of ultrasonication time was enough to obtain quantitative recovery. To spend minimum time, 3 minute of ultrasonication time was used for further work.

The influence of centrifugation time on the extraction efficiency of Au(III) in the developed procedure were examined at 4000 rpm between 1 and 9 min. The quantitative recovery was obtained with 3 minute of centrifuge time.

3.6. Study of interferences

The effects of matrix ions on extraction efficiency and on the selectivity of the developed method were also investigated by using the optimum conditions. A 10 mL model solution, which including 0.5 μg of Au(III) and different amounts of other ions, was prepared and the suggested extraction method was applied to the solution. The obtained results are shown in Table 1. The tolerance limits of matrix ions were taken as that value which caused a deviation of more than ±5 % in the recovery. Under the optimum conditions, no interference was observed from most of the ions tested except for Fe^{3+}, Cu^{2+}, Ni^{2+} and Mn^{2+} ions. In order to eliminate the interference effects of the ions, EDTA, NH_4F, KSCN, ascorbic acid and citric acid was checked. In the presence of KSCN, ascorbic acid and citric acid, the extraction of gold(III) was not possible. But, the interference effect of the ions can be eliminated by using 25 mg of EDTA and 75 mg of NH_4F as a masking agent.[3]

(Table 1. here)

3.7. Effect of the sample volume

The effect of sample volume on the extraction of Au(III) was investigated by using 10–40 mL of model solution keeping other conditions constant. It was found that the recovery of gold up to 15 mL of the sample solution were quantitative. Hence, a preconcentration factor of 60 was obtained using a final volume of 0.25 mL.

3.8. Analytical figures of merit

The analytical features of the developed method were evaluated under the optimum conditions. The whole preconcentration procedure could take about 10 min. It provides to simultaneously treat as many samples as can be placed in the centrifuge. Calibration curve constructed was $A = 4x10^{-3} +0.834C$ with a correlation coefficient ($R^2 = 0.996$). Where A is the absorbance and C is the gold concentration in µg L^{-1}. The limits of detection (LOD),which is defined as $C_{LOD} =3S_d/m$, (where C_{LOD}, Sd and m are the limit of detection, standard deviation of the eleven blank, and slope of a calibration graph, respectively) was 1.5 µg L^{-1}. The limit of quantification (LOQ) was found as 4.95 µg L^{-1} which calculated from the ratio of ten times the standard deviation of the eleven blank solutions to the slope of the calibration curve.

The preconcentration factor (PF), defined as the ratio of model solution to last volume was 60. The enhancement factor (EF), defined the slope ratio of calibration curve after and before preconcentration, was 51. The relative standard deviation (RSD) obtained from the microextraction procedure of 10 replicates of 10 mL solution containing 50 µg L^{-1} Au(III) was 4.2 %.

The consumptive index is the volume of samples necessary to attain a unit of preconcentration factor. The consumptive index (CI) can be found for practical purposes as: CI = Vs/ EF where Vs is the volume of sample solution (mL) consumed to achieve the EF value.[32] The CI was found 0.29.

3.9. Applications of the method

To prove the accuracy and applicable of the method, the developed microextraction method was applied to the determination of gold in CDN-GS-3D Gold Ore certified reference material. The obtained results of reference material in Table 2 agreed with the certified values.

(Table 2. here)

The accuracy of the suggested method was also verified by spiking various amounts of gold(III) in water and ore samples (Table 3). A good agreement was obtained between the added and recovered gold amounts. The all results obtained show that the suggested microextraction method was confidential and matrix independence for determination of gold in wide range of samples. The present SsLLME procedure was applied to the determination of gold in ore and rock samples obtained from Nigde and Erzincan (Table 4).

(Table 3. here)

(Table 4. here)

3.10. Comparison with other preconcentration techniques

The SsLLME- MS-FAAS method was compared with the other preconcentration methods used for the determination of gold in real samples in Table 5. The developed SsLLME- MS-FAAS method is environmental friendly with low usage of toxic organic solvents. The comparative data of different analytical characteristics showed that the obtained low detection limit and high enhancement factor of the proposed microextraction methodology are much better than other reported preconcentration methods for gold determinations in real samples.

(Table 5. here)

4. Conclusion

This study describes a novel and simple supramolecular solvent based liquid-liquid microextraction for preconcentration and separation of trace amounts of gold in ore samples prior to its determination by microsample introduction-flame atomic absorption spectrometry (FAAS). The important properties of the developed method: (I) it offers a simple and rapid alternative to conventional sample preconcentration methods, (II) decrease the consumption of toxic organic solvents and amount of secondary toxic waste, (III) It is free from matrix interference which are associated with gold in its natural occurrence. The suggested method was successfully applied for determination of low concentrations of gold in water, rock and ore samples with good accuracy and precision.

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Figure captions

Figure 1. Graphical representation of supramolecular solvent based liquid-liquid microextraction method (SsLLME)

Fig. 2. Effect of the pH on the extraction efficiency of Au(III) (N=3, 1-Decanol volume= 100 µL, THF volume=600 µL, Amount of complexing agent= 0.1 mg).

Fig. 3. Effect of the volume of THF on the extraction efficiency of Au(III) (N=3, pH= 6.0, 1-Decanol volume=50 µL, Amount of complexing agent= 0.1 mg).

Fig. 4. Effect of the amount of 1,3,4-thiadiazole-2,5-dithiol on the extraction efficiency of Au(III) (N=3, pH= 6.0, 1-Decanol volume= 50 µL, THF volume=200 µL).

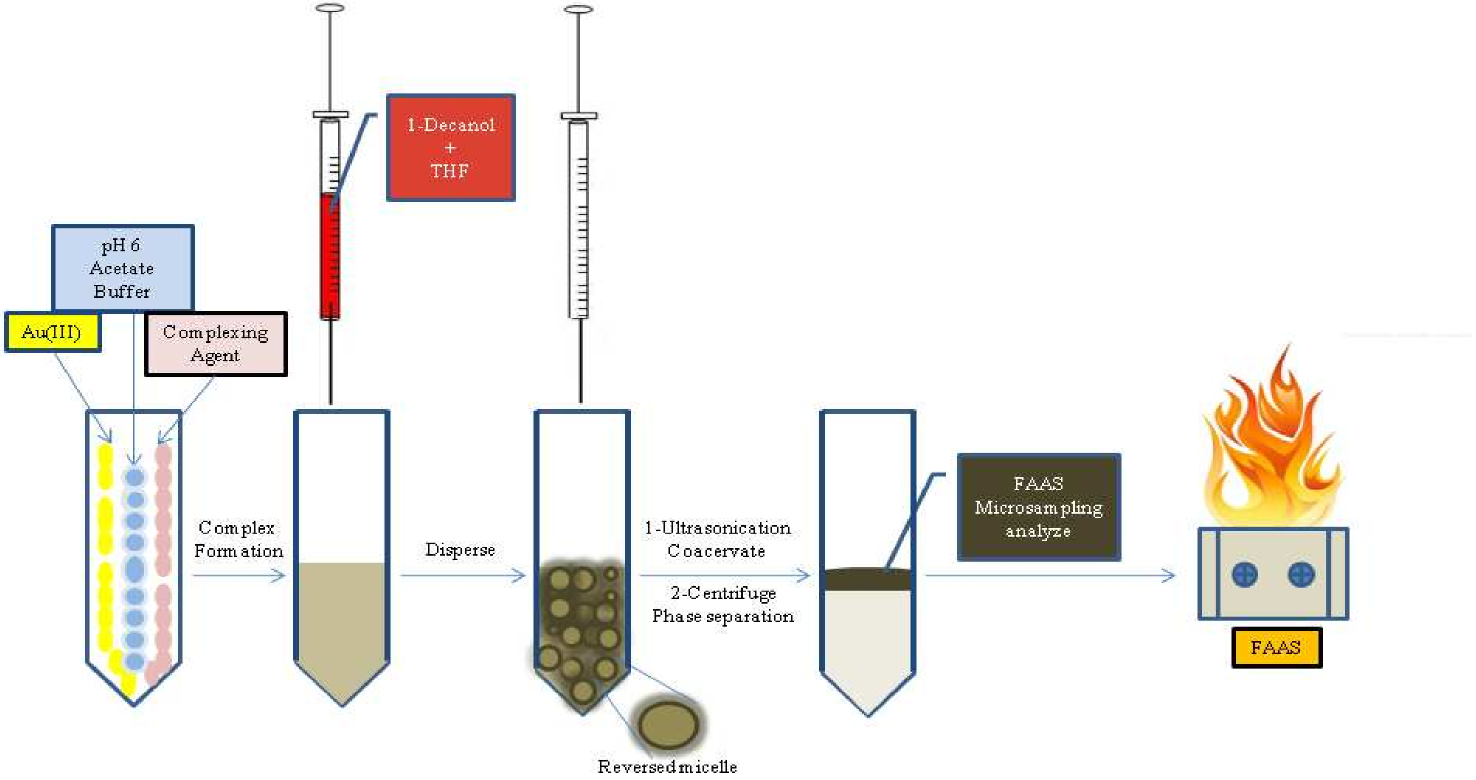
pH 6
Acetate
Buffer
Au(III)
Complexing
Agent
Complex
Formation
1-Decanol
+
THF
Disperse
1-Ultrasonication
Coacervate
2-Centrifuge
Phase separation
Reversed micelle
FAAS
Microsampling
analyze
FAAS

Fig. 1.

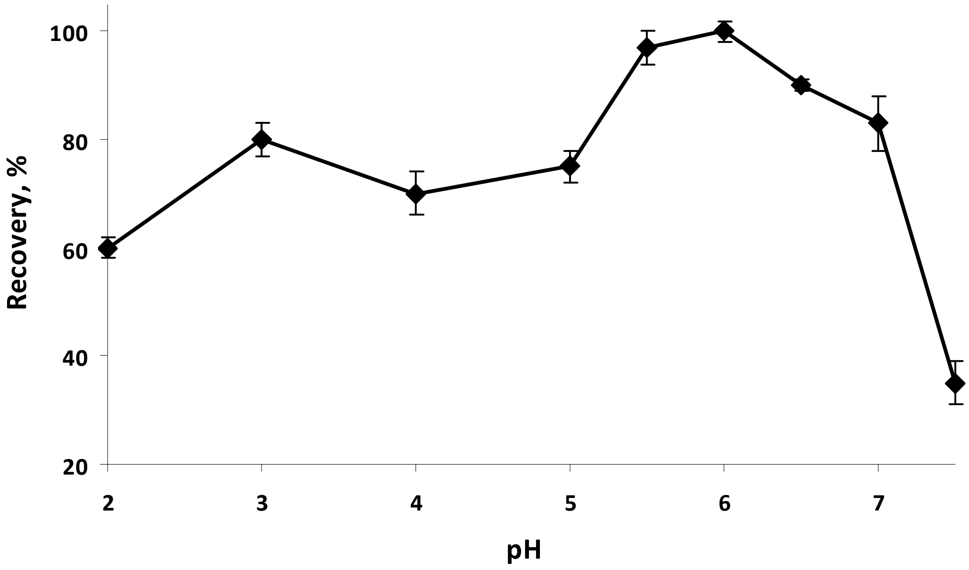

Fig. 2.

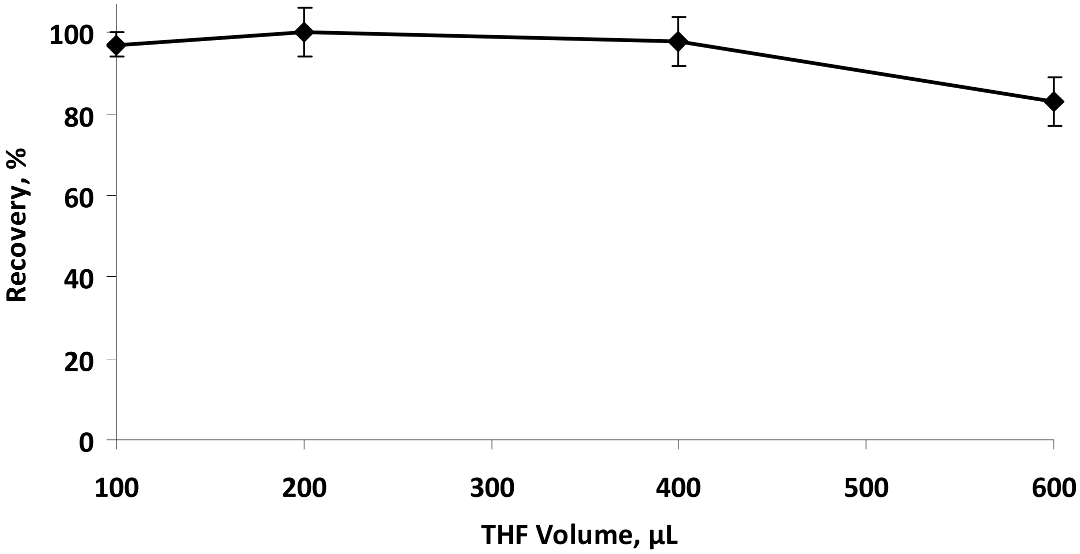

Fig. 3.

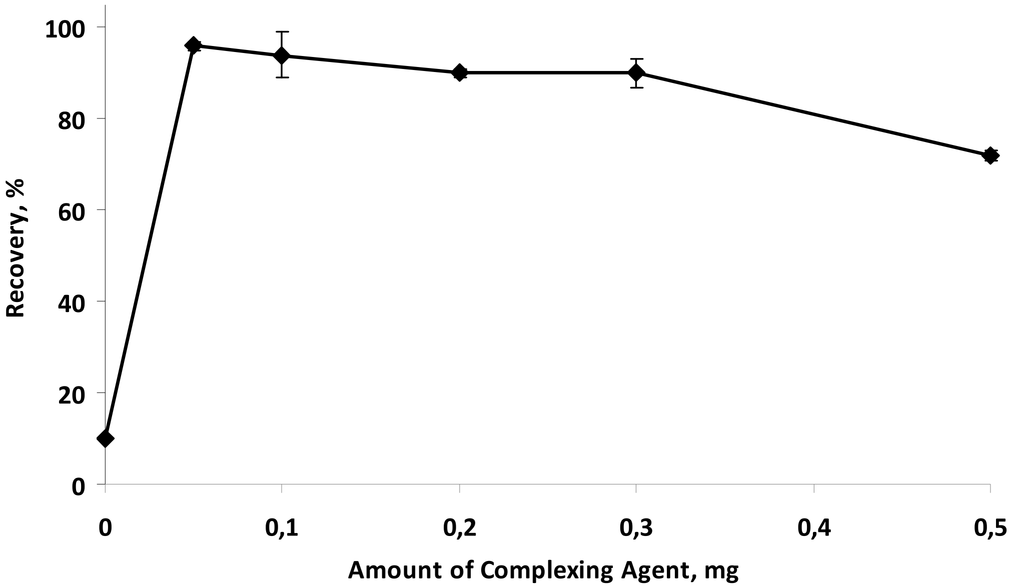
100
80
60
40
20
0
Recovery, %
0
0,1
0,2
0,3
0,4
0,5
Amount of Complexing Agent, mg

Fig. 4.

Table1. Effect of some matrix ions on the extraction efficiency of Au(III) (N=3).

Ion	Added as	Concentration, mg L^{-1}	Recovery, %
Na^+	$NaNO_3$	50000	97±5
K^+	KCl	50000	99±5
Mg^{2+}	$Mg(NO_3)_2.6H_2O$	500	103±4
Ca^{2+}	$Ca(NO_3)_2.4H_2O$	500	95±5
Zn^{2+}	$Zn(NO_3)_2.6H_2O$	5	100±3
Cr^{3+}	$Cr(NO_3)_3.9H_2O$	10	96±3
Pd^{2+}	$Pd(NO_3)_2$	2.5	97±1
Co^{2+}	$Co(NO_3)_2.6H_2O$	2.5	99±4
Cl^-	NaCl	77000	97±5
Fe^{3+}	$Fe(NO_3)_3$ $9H_2O$	100 [a]	95±0
Cu^{2+}	$Cu(NO_3)_2.3H_2O$	50 [b]	99±2
Mn^{2+}	$Mn(NO_3)_2.4H_2O$	50 [b]	98±0
Ni^{2+}	$Ni(NO_3)_2.6H_2O$	10 [b]	100±1

[a] Masked with 75 mg NH_4F.

[b] Masked with 25 mg EDTA.

Table 2. The analysis results of CDN-GS-3D Gold ore certified reference material (N: 5).

Certified Value (µg g^{-1})	Found (µg g^{-1})	Recovery, %
3.41 ± 0.25	3.38 ± 0.2	99

[a] Mean ± standard deviation.

Table 3. Addition and recovery test for microextraction of Gold(III) in water and ore samples (n=5).

	Added, µg	**Found, µg**	**Recovery, %**
Tap water from Canakkale	0.0	[a] <LOQ	-
	2.0	2.08±0.00[b]	104
	4.0	4.04±0.18	100
Well water from Sivas	0.0	<LOQ	-
	0.75	0.77±0.05	102
	1.5	1.47±0.08	98
Ore sample from Ordu	0.0	<LOQ	-
	0.75	0.78±0.07	103
	1.5	1.48±0.07	99
Ore sample from Samsun	0.0	<LOQ	-
	1.0	1.04±0.03	104
	2.0	1.90±0.03	95
Ore sample from Ordu-2	0.0	<LOQ	-
	0.75	0.72±0.02	96
	1.5	1.51±0.10	100

[a] LOQ: Limit of quantification.

[b] mean ± standard deviation.

Table 4. The application of presented method for gold level of ore and rock samples (N= 5).

Sample	**Concentration, µg g^{-1}**
Ore Sample from Nigde-1	1.73 ± 0.16
Ore Sample from Nigde-2	3.35 ± 0.25
Rock Sample from Erzincan-1	0.35 ± 0.06
Rock Sample from Erzincan-2	[a] <LOQ
Rock Sample from Erzincan-3	<LOQ

[a] LOQ: limit of quantification.

[b] Mean ± standard deviation.

Table 5. Comparison of the IL-DMME with other methods for the determination of gold

Method	LOD (μg L^{-1})	PF	Samples	Ref.
SPE-FAAS[a]	1.61	31	Water, soil, sediment	[1]
SPE-FAAS [a]	16.6	200	Water, soil, ore	[2]
CPE–FAAS [b]	3.8	16	ore	[33]
USAE-SFODME–FAAS [c]	0.45	34.8	Pharmaceutical, water	[34]
LLE- spectrophotometric [d]	0.5	200	Water, Ore	[35]
ILME-FAAS [e]	3.4	40	Water, soil	[7]
SsLLME-FAAS [f]	1.5	60	Water, Ore	This work

[a] Solid phase extraction-Flame atomic absorption spectrometry

[b] Cloud point extraction- Flame atomic absorption spectrometry

[c] Ultrasound-assisted emulsification of solidified floating organic drop microextraction- Flame atomic absorption spectrometry

[d] Liquid liquid extraction- UV-VIS spectrometry

[e] Ionic liquid microextraction-Flame atomic absorption spectrometry

[f] Supramolecular solvent based liquid-liquid microextraction-Flame atomic absorption spectrometry