A surfactant-based emulsification microextraction (SBEME) method for the atomic absorption determination of gold

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ABSTRACT

This work presents, a simple and quick method derived from surfactant-based emulsification microextraction to determine gold ions in environmental samples by using flame atomic absorption spectrometry (FAAS). Cetyltrimethylammonium bromide (CTAB) is used as a cationic surfactant agent in the extraction procedure. According to this method, the extraction solvent was dispersed into aqueous samples, and emulsification had occurred with the assistance of hand rinsing. The ion pairs formed between $AuCl_4^-$ and CTAB is extracted into the chloroform phase without the use of a dispersive solvent. Several experimental parameters such as effect of pH, concentration of the surfactant, etc. were investigated. The calibration curve was found to be linear in the range from 4 to 500 $\mu g\ L^{-1}$, the limit of detection was 1.1 $\mu g\ L^{-1}$ and the enrichment factor was 80. The relative standard deviation for 10 replicates was observed to be 2.2% with 25 $\mu g\ L^{-1}$ of gold. The quantitative recoveries of gold in water and ore samples were in the range of 96%–99%. The results show that this microextraction procedure is a selective, rapid, simple and low-cost method for the separation/preconcentration of gold in water and ore samples.

Keywords: Cetyltrimethylammonium bromide; FAAS; Water and ore samples

1. Introduction

Gold is a transition metal widely distributed in the nature at very low abundance (4 $\mu g\ g^{-1}$). It is one of the most precious metal being used in industry, commercial applications, jewelry and medical science due to its unique chemical properties, such as corrosion resistance, high ductility and electrical conductivity [1]. Gold content of 0.05 and 0.2 mg L^{-1} was found in sea water and river water, respectively [2]. Gold exists predominantly in two oxidative forms in the environment, which are Au(I) and Au(III). Trivalent gold compounds are more reactive than the univalent form of gold. Gold is stable in air and unreactive in the presence of most reagents. It is used widely in electrical contacts and computer technology due to its an excellent electrical conductivity [3,4]. No substantial arguments are available to show that gold compounds present a carcinogenic risk to humans, because gold salts are reduced to metallic gold in the human body and not absorbed into the organs. Nevertheless, some of the probable allergic effects of gold have been researched on the human body [5].

Gold mining, metal industries and jewelry manufacture are the main sources of gold exposure for the general population [6]. Most people are in constant contact with gold throughout their daily lives. For this reason, the determination of gold ions in environmental samples is of great concern. Flame atomic absorption spectrometry (FAAS) [7], electrothermal atomic absorption spectrometry (ETAAS) [8], and inductively coupled plasma mass spectroscopy (ICP-MS) [9] are widely used analytical techniques to determine gold concentrations. The FAAS is especially preferred because of its ease of use and low cost. Despite

good developments in the modern analytical instruments, the determination of gold is a challenge due to the very low concentrations in environmental samples, and the high concentration of interfering effects. Therefore, rapid and efficient preconcentration methods are needed for the preconcentration of trace amount of gold [10]. Coprecipitation [11], solvent extraction [12] and solid-phase extraction [13] are a few of the common methods for separating gold ions from the matrix media. However, these techniques have a few disadvantages such as the use of large amounts of organic solvents, time-consuming, and large secondary amount of waste [14]. In recent years, there has been great interest in analytical chemistry on the miniaturization of sample preparation [15,16]. The microextraction procedures including liquid phase microextraction (LPME) [17], solid phase microextraction (SPME) [18] and dispersive liquid–liquid microextraction (DLLME) [19] have been used for monitoring of metals and organic matter in environmental samples.

In the present study, a sensitive and selective surfactant-based emulsification microextraction (SBEME) procedure for the preconcentration of gold ions in water samples and ore samples has been developed. The cationic surfactant cetyltrimethylammonium bromide (CTAB) was used in the microextraction procedure for the selective separation of gold ions in the presence of different cationic and anionic species. In this procedure, gold is present in the form of anionic chlorocomplex ($AuCl_4^-$) which can interact with CTAB forming the corresponding ion pair which is extracted to organic solvent, then determined with FAAS.

2. Materials and methods

2.1. Apparatus and reagents

A PerkinElmer (Norwalk, CT, USA) A Analyst model 400 Flame Atomic Absorption Spectrometer (FAAS) was used in this study. Air (17 L min^{-1})-acetylene (2.5 L min^{-1}) gases were used for all the absorption measurements. A deuterium (D_2) lamp was used for background adjustment. A PerkinElmer hollow-cathode lamp was used as a light source for the gold element. For the solubilization process of the solid samples as well as the standard reference materials, a CEM Mars 6 One Technology (Matthews, USA) microwave solubilization system was used with a maximum pressure of 800 psi, a maximum temperature of 400°C, and 400 W of electric power. A Specord 210 Plus model spectrophotometer (Analytik Jena, Germany) was used to scan the absorption spectra of the ion pair Au-CTAB.

Throughout the experiments, a Merck-Millipore Direct-Q 8UV ultra pure water system was used for the preparation of solutions and the sterilization of glass equipment. Socorex (Socorex Isba SA, Switzerland) automatic micropipettes (20–200 µL, 100–1,000 µL, 1,000–5,000 µL) were used in the preparation of the model solvents in their appropriate concentrations. A Whatman NC-10 (0.45 µm) cellulose nitrate membrane was used to filter the environmental water samples, a Hanna pH-211 model (HANNA instruments, Romania) pH meter was used to determine the pH values in the aqueous solutions, and a Sigma 3-16P model centrifuge device (Sigma Laborzentrifugen GmbH, Germany) was used to accelerate a convenient organic phase.

All chemicals used were analytical reagents from either Merck Company (Darmstadt, Germany) or Sigma-Aldrich (GmbH, Steinheim, Germany). A stock solution of gold (1,000 mg L^{-1}) was prepared by diluting an appropriate amount of $HAuCl_4$ (Merck). The required pH adjustments were carried out using hydrochloric acid (HCl, Merck) and sodium hydroxide (NaOH, Merck). Chloroform ($CHCl_3$, analytical grade), dichloromethane (CH_2Cl_2, analytical grade), carbon disulphide (CS_2, for spectroscopy) and ethanol (C_2H_5OH, Merck) were used for the experiments. Stock solutions of 1×10^{-3} mol L^{-1} cationic surfactant CTAB (GmbH, Steinheim, Germany) were prepared fresh by dissolving an appropriate amount of the reagent in the pure water. The sandy soil reference material (CRM-SA-C) was purchased from High-Purity Standard Inc. (Charleston, South Carolina, USA).

2.2. SBEME procedure

A 40 mL sample volume including 25 µg L^{-1} of gold ions was placed in a 50 mL test tube and pH of the solution was adjusted by adding HCl (pH = 1). Furthermore, a 100 µL volume of the CTAB (1×10^{-3} mol L^{-1}) and 400 µL of extraction solvent ($CHCl_3$) was added into the solution with a tip by using 1,000 µL micropipette. The tube was manually shaken for a few seconds, for a white suspension solution to occur. In this step, gold ions reacted with CTAB and, were extracted into fine droplets of chloroform phase. TThe solution was centrifuged for 3 min at 2,000 rpm and the organic solvent droplet was formed under of the aqueous solution due to its high density. Afterwards, the water phase was removed by a pipette. The chloroform phase was diluted to 500 uL with ethanol (including 0.1 molar nitric acid) and the gold content was determined by FAAS.

2.3. Sample preparation

In this study, sea and stream water samples were collected from the Black Sea city, in the Trabzon, Turkey. The water samples were filled into polyethylene containers and then acidified with 0.1 mol L^{-1} HNO$_3$ in order to block any potential breakdown of metal ions. Finally, 40 mL of the water samples were filtered though a 0.45 mm cellulose membrane filter and the microextraction procedure was applied to determine the gold content using FAAS.

For the solid sample analysis, the ore samples were collected from Akoluk (Ordu, Turkey), Mastra (Gümüşhane, Turkey) and Keletaş (Gümüşhane, Turkey). The standard reference material (CRM) and the ore samples were dissolved using a closed microwave digestion system. For this purpose, the ore samples and the standard reference material were sensitively weighed at 0.06 g and placed into polytetrafluoroethylene vessels. 1.5 mL of HCl, 5 mL of HNO$_3$ and 1 mL of H_2O_2 were added into the vessels. After digestion process, the remaining acidic solution was heated on a hotplate to obtain a nearly dry suspension. Pure water was added to the solution (30 mL) which was then filtered with a cellulose membrane (0.45 µm). Lastly, the final volume was diluted to 40 mL using ultra pure water, developed procedure (Section 2.2) was applied to this solution in order to determine the gold concentration.

3. Results and discussion

3.1. Record of CTAB-Au by spectrophotometric study

In this section, the complexation affinity of CTAB with Au(III) was examined by using UV-visible spectroscopy in water/chloroform solvent system. An aliquot volume of a solution containing 25 µg L^{-1} Au(II) and 100 µL of (5×10^{-6} mol L^{-1}) was transferred into a plastic tube and the previously presented method (Section 2.2) was applied. After the extraction procedure, the final volume of organic phase was diluted to 500 µL using ethanol, and then transferred into the 0.5 cm quartz cell to scan from 200 to 800 nm at 1 nm intervals in Fig. 1. Moreover, the blank absorbances performed on the sample blank were without the presence of Au and CTAB.

3.2. Optimization of the analytical parameters for the analysis of the gold

In this research, a simple, quick, and sensitive method based on the principle of an emulsification microextraction process was developed. $AuCl_4^-$ ions reacted with a cationic surface-active agent (CTAB) and this corresponding ion pair extracted in an organic phase at pH 1. The reaction is given:

$$AuCl_{4\ (aq)}^- + CTAB_{(aq)} + Chloroform \rightarrow [(AuCl_4^-).(CTAB)]_{Chloroform}$$

Acidity is one of the most important factors on the metal–chelate formation and the subsequent extraction. The influences of the hydrochloric acid on the quantitative recovery of gold ions at the microextraction procedure were investigated at the molarity range of 0.1–5. As can be seen from Fig. 2a, Au ions were effectively recovered at acidic conditions; however the results were not quantitative at 5 mol L^{-1}. This maybe because of breakdown of the surfactant agent in high acidic conditions. We also studied pH effect on the SBEME method in the range from 2 to 8. In Fig. 2b, the signal intensity of Au dramatically decreased after pH 3; this is because, at high pH values, $AuCl_4^-$ compound breaks up leading to the production of free state of gold ion that cannot react with the cationic surfactant. As a practical reason, 0.1 mol L^{-1} of HCl (pH = 1) was limited throughout the experiments.

Besides the acidity of the solution, the concentration of the surfactant also plays an important role in the formation of $AuCl_4^-$ complex anion. The effect of the CTAB agent (1×10^{-3} mol L^{-1}) volume was studied in the range 50–400 µL. Fig. 3 shows that, the extraction recovery was constant when the volume of the CTAB reagent was larger than 50 µL. At lower CTAB concentrations, the gold signal determined using the SBEME method was decreased. Thus, a CTAB volume of 100 µL was chosen for subsequent experiments.

The signal of the extracted ion pairs substantially depends on the nature and volume of the extraction solvent. The extractant phase should have lower or high density than water, low volatility and water solubility. In this work, the extraction capacity of some organic solvents such as carbon tetrachloride (CCl_4), chloroform ($CHCl_3$), dichloromethane (CH_2Cl_2) and carbon disulphide (CS_2) were tested. The results indicated that CS_2 and CH_2Cl_2 were formed an unstable cloudy solution and the sediments phases were difficult to remove from aqueous solution. On the other hand, the recovery results $CHCl_3$ between (98% ± 2.3 %) and CCl_4 (91% ± 2.1 %) had a few statistical differences. For the extraction solvent, $CHCl_3$ was selected for further experiments. The effect of the volume of chloroform on the extraction efficiency was studied. For this purpose, different volumes of chloroform (200–500 µL) were subjected to the 40 mL model solution in Fig. 4. The results indicated that the recoveries remained quantitative between 400 and 500 µL, and thus 400 µL of $CHCl_3$ was selected as the optimum volume.

The effect of concentration of ionic strength on the extraction efficiency of gold was also investigated in the range of 0–5 (w/v) of NaCl, under the optimum conditions. The results show that changing the ionic strength did not effect the extraction recovery in Fig. S1. These data indicated that the presented procedure is available to quantify gold content in saline solutions such as sea water.

In all extraction techniques, sample volume is one of the essential factors to obtain a high enrichment factor. In this work, the influence of the sample volume was studied in the range of 10–40 mL including 25 µg L^{-1} of gold, while the other parameters were kept constant in Fig. S2. The results showed that the extraction efficiency of gold ions was quantitative in the all sample volumes. Finally, a 40-mL sample volume was selected to obtain the best enrichment factor.

3.3. Effect of foreign ions

To show the selectivity of the presented method, the effects of coexisting ions in the recovery of gold ions were studied under optimized conditions. A 40 mL of solutions containing 25 µg L^{-1} Au^{3+} and different amount of other ions were prepared and performed according to the proposed procedure (Section 2.2). As can be seen in Table 1, the presence of large amounts of cations and anions in environmental samples do not have an interfere effect on the determination of gold with SBEME. Thus, the method shows excellent selectivity toward the gold ions.
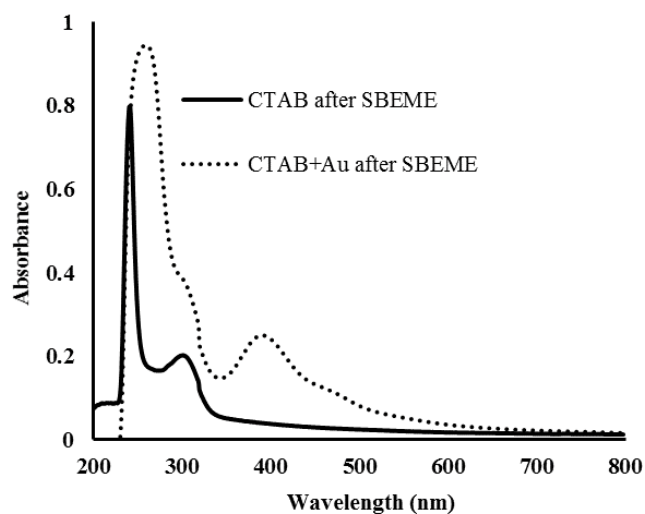

Fig. 1. Absorption spectra for the determination of Au with/without extraction. The SBEME conditions: Au, 25 µg L^{-1}; CTAB, 5×10^{-6} mol L^{-1}; $CHCl_3$, 400 µL; pH, 1; sample volume, 40 mL.
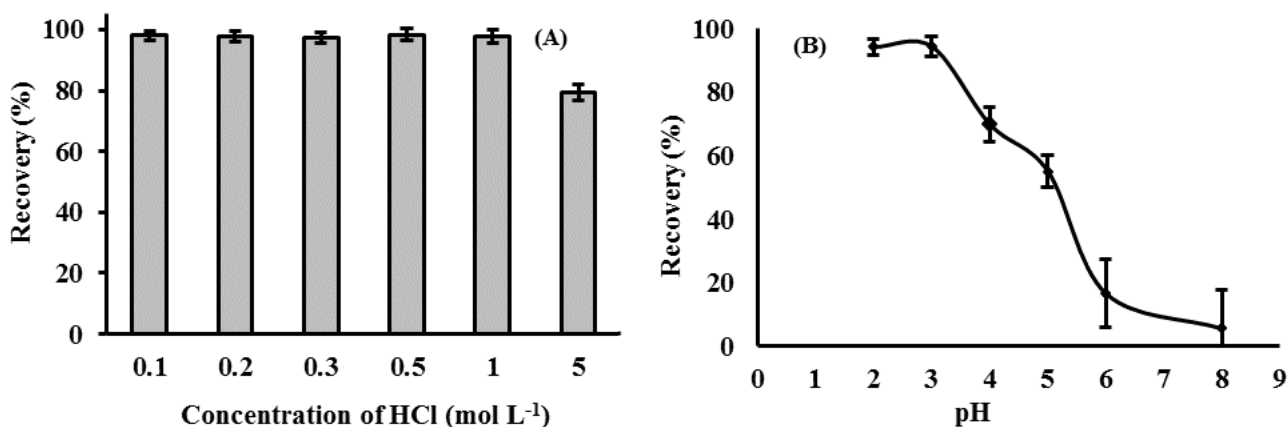
Fig. 2. (A) Effect of the concentration of HCl on the recovery of gold ions. (B) Effect of pH of the sample solution on the extraction efficiency of the gold. Gold concentration, 25 μg L^{-1}; sample volume, 40 mL; amount of CTAB, 100 μL (1 × 10^{-3} mol L^{-1}); volume of CHCl$_3$, 400 μL; centrifugation rate, 2,000 rpm; centrifugation time, 3 min; $N = 3$.

3.4. Analytical performance and comparison

Analytical parameters including the limit of detection (LOD) and the limit of quantitation, the calibration range and the precision (RSD, %) were obtained to evaluate the performance of the method. A calibration curve was defined by preconcentrating 40 mL of model solution. The calibration of gold was in the range of 4–500 μg L^{-1} with the regression equation of $A = 0.0028C_{(Au)} + 0.0038$ ($R^2 = 0.9997$) after the preconcentration procedure. Here, A = absorbance for Au in the enriched phase, $C_{(Au)}$: the gold concentration (μg L^{-1}) in the sample solution. The LOD (1.1 μg L^{-1}) was calculated by the formula LOD = $3s/m$ (whereby, s and m are the standard deviation of the blank and slope of the calibration graph, respectively) [20]. Blank signals obtained a 0.0025 ± 0.0009 absorbance value in FAAS as parallel to the measurements made for the calibration standards and sample solutions. The procedure was repeated ten times and the relative standard deviation in the determination of 5 and 25 μg L^{-1} of Au were 3.4% and 2.2%, respectively. The intra-and inter-day precisions of Au were checked and the results were nearly the same in the selected concentrations.

The preconcentration factor for the method is 80, calculated by the ratio of volumes of the sample (40 mL) and the final solutions (0.5 mL) in Eq. (1),

$$PF = \left(\frac{C_a}{C_{aq}} \right) \tag{1}$$

C_a and C_{aq} are the concentrations of analyte in the enrichment phase and aqueous phases, respectively. C_a was calculated according to the calibration graph of the standard solution of gold in the procedure.

A comparison of the current method with some reported preconcentration procedures in literature combined with different analytical techniques is given in Table 2. The aim of the manuscript was to study the feasibility of a SBEME preconcentration procedure combined with FAAS for trace gold in water and ore samples. There are a number of papers concerning with the topic of gold determination but, as far
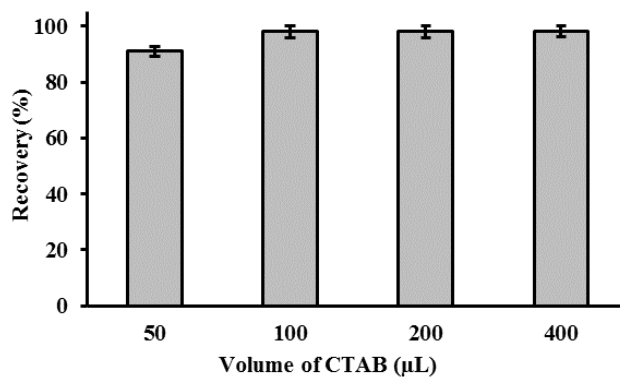

Fig. 3. Effect of CTAB (1 × 10^{-3} mol L^{-1}) concentration on the recoveries of gold ions. Experimental conditions: pH, 1; 400 μL CHCl$_3$; sample volume, 40 mL; $N = 3$.

as we know, this is the first time that the combination of cationic surfactant (CTAB) combination with FAAS was used in the microextraction procedure. The presented method has significant advantages with respect to extraction of gold ions from aqueous solution to organic phase. Shaking of the solution for a few seconds produces a cloudy white suspension without the addition of extra complexing agent or disperser solvent. In addition, the proposed methodology involves very low consumption of reagents and consumables, easily operated, high selectivity towards gold ion and speed. Despite the fact that limits of detection obtained by the developed method (1.1 μg L^{-1}) are higher with those reported by TXRF, ETAAS and ICP-OES systems, this LOD is similar when compared with FAAS detections in Table 2. Thus, the presented method could be of great interest especially for gold determination in routine laboratories using a low-cost FAAS instrument.

3.5. Application of the real sample

In order to establish the validity of the microextraction, the certified reference material (CRM-C-Sandy Soil C), was

analyzed for gold. The determined level of 24.5 ± 0.8 μg g^{-1} is within tolerance of the certified value of 25 μg g^{-1}. The standard addition method was used to check the accuracy of the method that different amounts of gold were added to

Table 1
Effect of foreign ions on the extraction of gold (25 μg L^{-1}) with SBEME

Coexisting ion	Concentration (mg L^{-1})	Au recovery (%)
Na^+	20,000	98 ± 2
K^+	20,000	97 ± 3
Ca^{2+}	1,500	97 ± 3
Mg^{2+}	1,500	97 ± 2
Al^{3+}	50	99 ± 2
Zn^{2+}	50	98 ± 3
Co^{2+}	50	97 ± 3
Cr^{3+}	50	98 ± 2
Mn^{2+}	50	98 ± 2
Ag^+	50	97 ± 2
Pd^{2+}	50	97 ± 2
Fe^{3+}	50	99 ± 2
Pt^{2+}	50	98 ± 3
NO_3^-	1,500	96 ± 2
PO_4^{3-}	1,000	96 ± 2
SO_4^{2-}	1,000	96 ± 3
Mixed[a]	20	97 ± 2

[a]Ni, Co, Cr, Zn, Pb, Cd, Mn, Ni, Se, Co, Cr, V, Mo, Zn, Cu, Fe.
Conditions: pH, 1; sample volume, 40 mL; amount of CTAB, 100 μL of 1×10^{-3} mol L^{-1}

Table 2
Analytical procedures published for gold determination

Fig. 4. Effect of $CHCl_3$ volume on the extraction of gold ions. Experimental conditions: pH, 1; 400 μL $CHCl_3$; sample volume; 40 mL; $N = 3$.

the solid and water samples. As mentioned in Table 3, in the recovery experiments, good results were obtained for all the samples. The results indicate that the SBEME-FAAS combination is excellent for the preconcentration and determination of gold in environmental samples in Table 4.

4. Conclusions

In this study, a sensitive analytical methodology based on solvent emulsification for preconcentration and determination of gold in different water and solid samples using a cationic surface active reagent was developed. CTAB reacting with gold ion showed perfect performance in the extraction of gold ions without using any disperser solvent. The selectivity of the CTAB was checked towards gold ions by examining a series of trace metal ions, including manganese(II),

Technique	Extractant	LOD (μg L^{-1})	EF/PF	Sample	Ref.
M-CIAME-UV-vis	TMK	0.7	28	Mineral and water	[21]
SsLLME-FAAS	TDAD	1.5	60	Water and ore	[22]
SPE-FAAS	Dowex M	1.61	31	Water, soil, sediment and ore	[23]
CPE-FAAS	PMBP	3.8	16	Mine	[24]
SPE-UV-Vis	DCHNAQ	6.1	100	Water, jewel, ore	[25]
USAE-SFODME-FAAS	ACABPP	0.45	34	Water, pharmaceutical and synthetic samples	[26]
DLLME-ETAAS	ACABPP	0.0048	48.7	Water and hair	[27]
SPE-ICP-AES	DCC	0.16	–	Ore and rock	[28]
DLLME-ETAAS.	DHA	0.002	60	Alloy	[29]
IL-LME-FAAS	[C_4MIM][PF_6]	72	10	Water	[30]
LL-SAEME-TXRF	CTAB	0.05	–	Water	[31]
SBEME-FAAS	CTAB	1.1	80	Water and mine	This work

SsLLME: Supramolecular solvent microextraction, SPE: Solid-phase extraction, CPE: Cloud point extraction, UV-Vis: Ultraviolet–visible spectroscopy, USAE-SFODME: Ultrasound-assisted emulsification of solidified floating organic microextraction, DLLME: Dispersive liquid–liquid microextraction, LL-SAEME: Ligandless surfactant-assisted emulsification microextraction, IL-LME: Ionic liquid–liquid microextraction, TMK: Thiomichlersketone, TDAD: 1,3,4-thiadiazole-2,5-dithiol, PMBP: 1-phenyl-3-methyl-4-benzoyl-5-pyrazolone, DCC: N,N′-dicyclohexyl carbodiimide, C_4MIM][PF_6]: 1-butyl-3-methylimidazolium hexafluorophosphate, DCHNAQ: 2,3-dichloro-6-(3-carboxy-2-hydroxy-1-naphthylazo)quinoxaline, ACABPP: N-(4-{4-[(anilinocarbothioyl)amino]benzyl}phenyl)-N-phenylthiourea, FAAS: Flame atomic absorption spectrometry, ICP-AES: Inductively coupled plasma atomic emission spectroscopy, ETAAS: Electrothermal atomic absorption spectroscopy, TXRF: Total reflection X-ray fluorescence, EF: Enrichment factor, PF: Preconcentration factor.
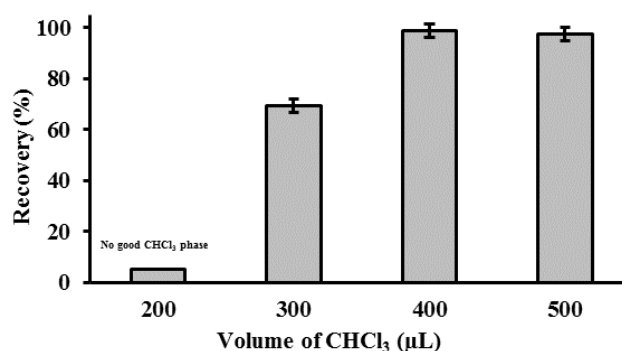
Table 3
Spiked recoveries of gold ions in water and ore samples using optimal experimental conditions (sample quantity for solid and water, 0.06 g and 40 mL, respectively; final volume, 0.5 mL; N = 3)

Sample	Added, Au (µg)	Found, Au (µg)	Recovery (%)
Sea water	0.00	<LOD	–
	0.50	0.49 ± 0.01	98 ± 1
	1.00	0.99 ± 0.02	99 ± 2
Stream water	0.00	<LOD	–
	0.50	0.49 ± 0.01	98 ± 1
	1.00	0.98 ± 0.02	98 ± 2
River water	0.00	<LOD	–
	0.50	0.48 ± 0.01	96 ± 2
	1.00	0.98 ± 0.02	98 ± 2
Kaletaş ore	0.00	0.45 ± 0.02	–
	0.50	0.94 ± 0.02	98 ± 2
	1.00	1.43 ± 0.02	98 ± 2
Akoluk ore	0.00	1.27 ± 0.02	–
	0.50	1.75 ± 0.03	96 ± 2
	1.00	2.25 ± 0.03	98 ± 2
Mastra ore	0.00	4.33 ± 0.02	–
	0.50	4.81 ± 0.02	96 ± 2
	1.00	5.29 ± 0.03	96 ± 2

Table 4
Gold content in solid and liquid samples after SBEME procedure

	Water samples (µg L⁻¹)			Solid samples (µg g⁻¹)		
	Sea water	River water	Stream water	Kaletaş	Akoluk	Mastra
Au	n.d	n.d	n.d	7.5 ± 0.2	21.2 ± 0.9	72.2 ± 2.9

n.d: Not detected.

palladium(II), nickel(II), cadmium(II), cobalt(II), iron(III), copper(II), lead(II) and zinc(II) in the SBEME procedure. Advantages of the method are simple, rapid and minimized waste generation. The SBEME approach associated with FAAS detection can readily determine gold(III) at trace level in solid and water samples with good preconcentration factor, low cost, high selectivity and short extraction time.

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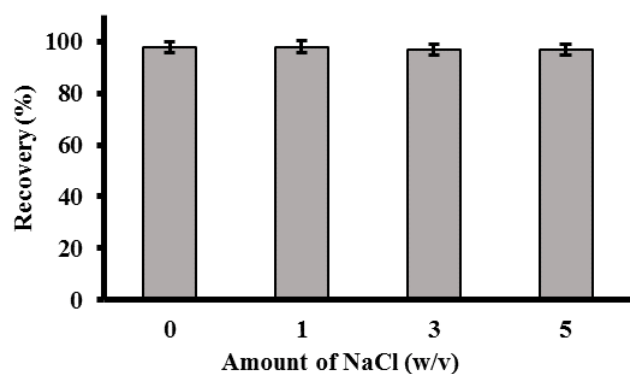
Supplementary information:

Fig. S1. Effect of ionic strength on the extraction of gold ions obtained from SBEME. pH, 1; concentration of CTAB, 5×10^{-6} mol L^{-1}; sample volume, 40 mL; $N = 3$.
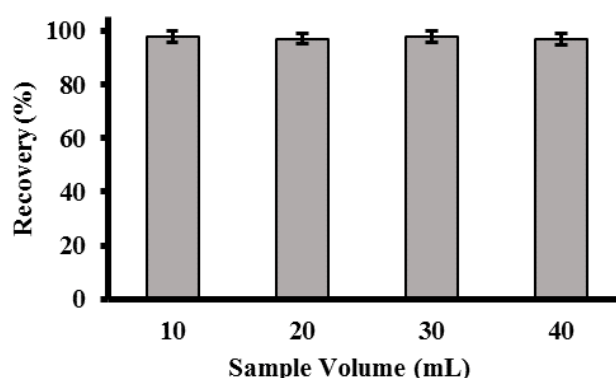
Fig. S2. Effect of sample volume on the recovery of Au(III) ions. Au, 25 µg L^{-1}; CTAB, 5×10^{-6} mol L^{-1}; CHCl$_3$, 400 µL; pH, 1; sample volume, 40 mL; ($N = 3$).