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Ion-association dispersive liquid–liquid microextraction of ultra-trace amount of gold in water samples using Aliquat 336 prior to inductively coupled plasma atomic emission spectrometry determination

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Abstract

Background: Gold is a rare and noble metal with atomic number of 79. Several techniques including both spectrometric and electrochemical methods are widely used to determine gold level in real samples. As a result of low concentration of gold in environmental samples, sample preparations such as extraction, clean-up, and pre-concentration before instrumental analysis are mandatory. Thus, a pre-treatment method (dispersive liquid–liquid microextraction (DLLME)) for gold pre-concentration and inductively coupled plasma optical emission spectrometry (ICP-OES) determination is proposed.

Methods: An extraction method employing DLLME and ICP-OES has been developed for rapid separation, pre-concentration, and determination of ultra-trace amount of Au (III). The extraction of the analyte was performed in the presence of a quaternary ammonium cation, *N*-methyl-*N*,*N*,*N*-trioctylammonium chloride, (Aliquat 336) as an extractant based on ion-association extraction system.

Results: 1-Octanol and acetonitrile were used as extraction and disperser solvents, respectively. The variables affecting the extraction conditions were optimized. A calibration curve in the range of 0.3–100 ng mL^{-1}, the detection limit of 0.09 ng mL^{-1}, an enrichment factor of 150, and an extraction recovery of 74 % were obtained. The precision (RSD %) of the method was 6 % for five replicates and recoveries of 10 ng mL^{-1} Au(III).

Conclusions: The combined DLLME method with ICP-OES can readily determine Au(III) at trace (μg L^{-1}) level using only 10 mL of sample solution (tap, lake, and mining water) without interference by the matrices. This methodology is simple, fast, and low cost which can be used in routine analytical laboratories.

Keywords: Gold, Dispersive liquid–liquid microextraction, Aliquat 336, Inductively coupled plasma atomic emission spectrometry

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Background

Gold is a rare and noble metal with atomic number of 79 and 14 radioactive isotopes with half-times from a few seconds to a few days (Aitio et al. 2014). The word noble refers in part to its rarity, beauty, and wide utility in economic and industrial activity due to its chemical stability, high ductility, corrosive resistance, and low impedance (Kagaya et al. 2010). The average concentration of gold in earth's crust is approximately 4 µg kg^{-1} (ppb) and the values of 0.05 and 0.2 ng mL^{-1} (ppb) were found in sea water and river water, respectively (Lee 1996; Rancis et al. 2005). Several techniques including both spectrometric and electrochemical methods are widely used to determine gold in real samples (Shamsipour and Ramezani 2008; Gomez and McLeod 1993; Ye and Beng khoo 1999; Hu et al. 2006; de-Souza Periera et al. 2014; Ye et al. 2014). As a result of a low concentration of gold in environmental samples and matrix interferences, the limiting factor in the analysis is often the sensitivity of the method. Therefore, sample preparations such as extraction, cleanup and pre-concentration before instrumental analysis are mandatory. Solid-phase extraction (Zhang et al. 2011; Sabermahani et al. 2012; Iraji et al. 2013; Afzali et al. 2014; Kazemi et al. 2015), cloud-point extraction (Manzoori et al. 2007; Tavakoli et al. 2008), co-precipitation (Messerschmidt et al. 2000), and liquid–liquid extraction (LLE) (El-Shahawi et al. 2007; Vasilyeva et al. 1975; Ohava et al. 1995; Kolekar and Anuse 2001) are used for sample preparation purposes. LLE has been widely used for separation and pre-concentration of gold ions. This technique is based on transfer of desired analytes from the primary aqueous sample to water-immiscible solvent (Pena-Periera et al. 2009). Gold ion normally exists in an aqueous phase as a hydrated anion complex ($AuCl_4^-$) with little or no tendency to be transferred to organic phase. Suitable cations like quaternary ammonium cations (e.g., tetrabutylammonium), organometallic cations (e.g., Ph_3Sn^+), and cationic colorants (e.g., Rhodamine B) have been applied to form non-solvated ion-pair with $AuCl_4^-$ (Das and Bhatacharyya 1976) to produce extractable species. However, LLE is not without its associated problems such as being time consuming, large amount of toxic organic solvent consumption, and difficulty in automation. Recent trends in analytical chemistry are in the direction of simplification and miniaturization of sample preparation procedures as well as the minimization of solvent and reagent usage. So, dispersive liquid–liquid microextraction (DLLME) has been introduced for organic and inorganic analyte separation from aqueous matrices (Rezaee et al. 2006). DLLME is based on dispersion of extraction solvent in aqueous bulk samples assisted with a disperser solvent. Then, the analytes are allowed to be extracted into fine droplets of extraction solvent during the formation of cloudy solution (Anthemidis and Ionnp 2009). After centrifuging, the separated organic phase will be analyzed with appropriate techniques. The advantages of this technique include simplicity of operation, rapid extraction, and high-enrichment factors (E_f) (Leong et al. 2014). DLLME studies related to ion metals involve the use of complexing reagents, ligandless-dispersive liquid–liquid microextraction (LL–DLLME), and ion-pair forming agents. The two first approaches are widely used for different kinds of metals such as Pd (Mohammadi et al. 2010), Ag (Mohammadi et al. 2009a), and Cu (Mohammadi et al. 2009b) in the cationic form. The ion-pair-based approach has only been applied for gold following the formation of an ion-pair between $AuCl_4^-$ complex and different counterions such as Victoria Blue R, dicyclohexylamine, benzyldimethyl tetradecyl ammonium, and between $AuCN_2^-$ complex and Astra Phloxin (De La Calle et al. 2011; Kocuroua et al. 2010).

Because of high toxicity and limitation in extracting various analytes of commonly used extraction solvents, two different aspects (I) the use of new solvents, typically ionic liquids and (II) the expansion of the application scope using polar and low-density organic solvents such as long-chained alcohols or hydrocarbons are considered (Yana and Wanga 2013). In this study, a pretreatment method (DLLME) for Au determination with a quaternary ammonium salt, *N*-methyl-*N,N,N*-trioctylammonium chloride, (Aliquat 336) as an extractant reagent based on ion-association solvent extraction system is proposed. The purpose of the present work is to optimize various parameters affecting the efficiency of the combination of microextraction and ICP-OES for the determination of gold in water samples.

Methods

Reagents and solutions

Reagent grade 1-octanol, 1-dodecanol, acetonitrile, acetone, ethanol, NaCl, HCl, and HNO_3 were purchased from Merck chemical company (Darmstadt, Germany) and *N*-methyl-*N,N,N*-trioctylammonium chloride (Aliquat 336) was purchased from Sigma–Aldrich (USA). Doubly distilled deionized water was prepared by MiliQ water (Merck, Millipore) and was used in all experiments. A stock standard solution of gold as $AuCl_4^-$ and other trace and major elements (for interfering studies) (1000 µg mL^{-1}-SM 80B-500 VHG Labs-USA) were utilized and diluted to the desired concentration daily prior to use. Tap water (Karaj, Alborz province, Iran), lake water (Orumieh, West Azarbaijan, Iran), and mining water (Anguran mine, Zandjan province, Iran) samples were collected in acid-leached polyethylene bottles and acidified by HNO_3.

Instrumentation

In this study, a simultaneous radial viewing torch configuration ICP-OES (Varian 735-OES, Australia) equipped

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with charge-coupled device (CCD) detector has been used for the determination of gold. The control of the spectrometer is provided by PC-based ICP Expert II software. All measurements were carried out in time-scan mode at 242.8 nm ionic emission Au spectrum. A Vision VS 5500N Centrifuge (Korea) was used to speed up the phase separation.

General procedure

In a 10-mL volumetric flask, 3.5 mL concentrated HCl, 2.0 mL $AuCl_4^-$ solution (1.0 mg L^{-1}), and 0.5 g NaCl, salt were added and diluted to the mark with distilled water and transferred to a proper homemade test tube (final concentration of gold was 0.200 mg L^{-1}). Fifty microliters of 1-octanol as extraction solvent containing Aliquat 336 (0.1% w/v) and 1.5 mL acetonitrile as disperser agent was together rapidly injected to test solution by a disposable syringe. A cloudy solution (water/1-octanol-Aliquat 336/acetonitrile) was formed in the test tube where the $AuCl_4^-$ is extracted into fine droplet of 1-octanol by aid of Aliquat 336 as an ion-association agent. The mixture was then centrifuged for 10 min at 2900 rpm. After this process, the dispersed fine droplets were collected on the top of the solution in the neck of the homemade test tube. Finally, the collected organic phase (50 ± 3% (μL)) was introduced to ICP-OES instrument through four-channel peristaltic pump, and the gold content was determined in time-scan mode. When running organic samples by ICP-OES, a higher power level (1.6 KW) and lower nebulizer flow rate (0.6 L min^{-1}) are required to ignite and maintain plasma. With correctly chosen conditions, the intense green tongue generated by molecular emission of C2 and CN emission will be visible between the turns of the induction coil but will not extend above the top of the torch (Boorn and Browner 1982). So, the viewing height in this study was chosen 15 mm above the load coil to avoid background emission due to green tongue.
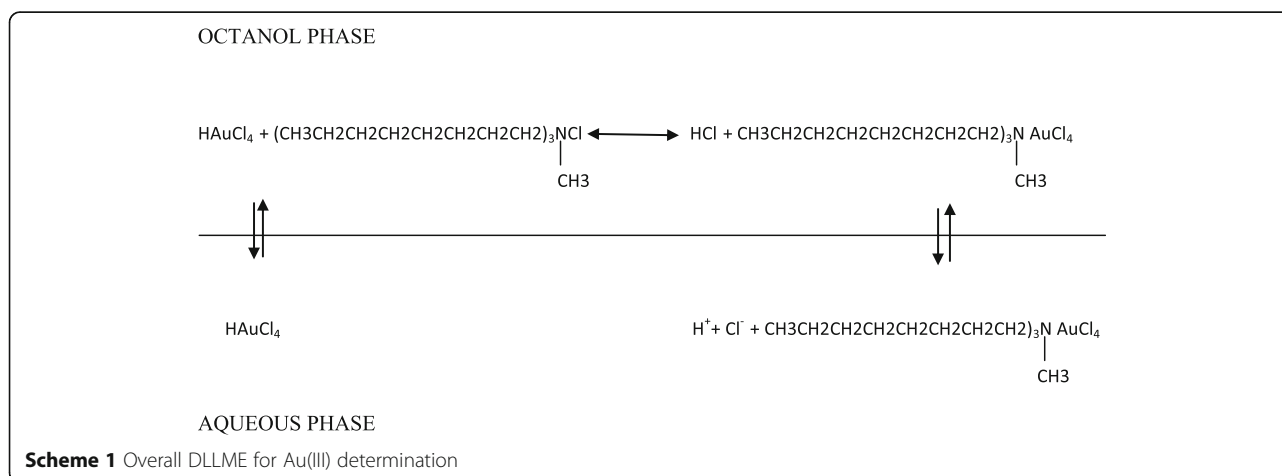
Preparation of water samples

Tap water sample from laboratory of applied geological research center of GSI (Karaj, Alborz province), Lake water as a source for hydro-geochemistry studies from Orumieh lake (Orumieh, West Azarbaijan province), and mining water from Anguran mine (Zandjan province) were collected in acid-leached poly(ethylene) bottles, filtered, and acidified with HNO$_3$ to prevent adsorption of metal ions on the bottle wall.
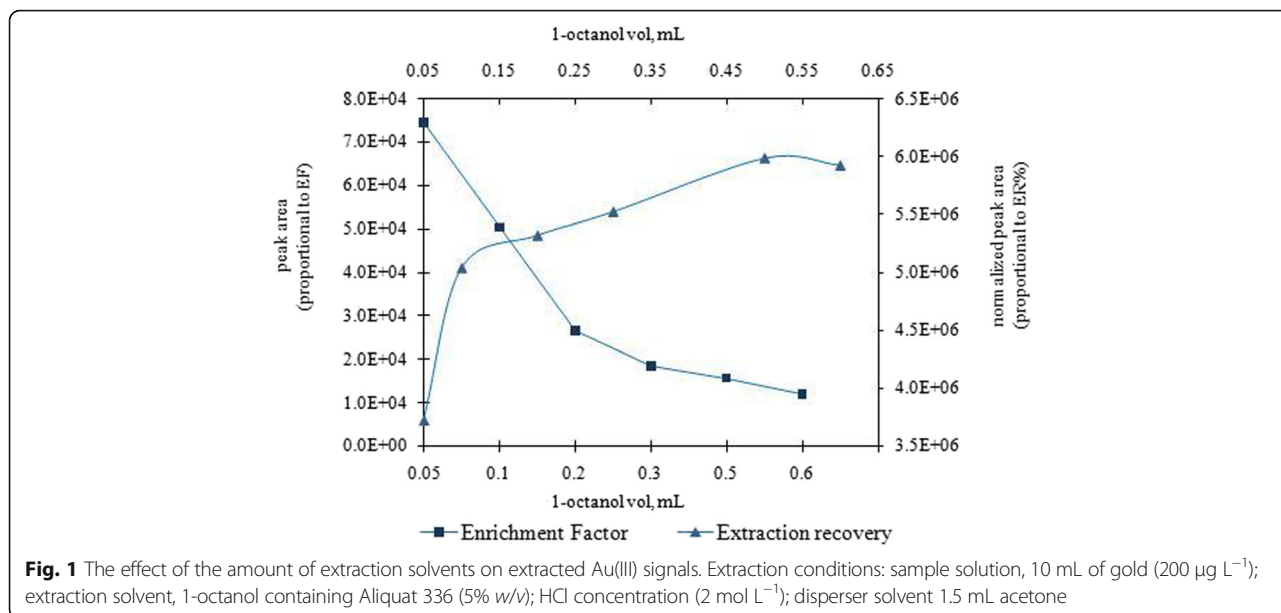
Preparation of certified reference material (CRM) samples

The proposed method was also applied to the extraction and determination of gold in three geochemical reference samples (GAU 15–17). An accurately measured sample (0.5000 g) of GAUs was dissolved in aqua regia. The solution was evaporated to near dryness to remove the nitrogen oxides. Then, 10 mL distilled water and a few drops of concentrated hydrochloric acid were added. The solution was filtered, and the filtrate was transferred completely into a calibrated 25-mL volumetric flask and diluted to the mark with water. The extraction and determination of gold content was carried out following the general procedure described.

Results and discussion

In order to achieve the optimized experimental conditions for high-enrichment factor and quantitative extraction of gold ions by Aliquat 336 through ion-association DLLME, the influence of some important parameters including concentration of ion-association agent (Aliquat 336), HCl concentration, salt concentration, and nature and volume of both extraction and disperser solvents were investigated. These surveys were done due to their effects on emission signal of gold extracted to organic phase. In general, the enrichment factor (E_f), extraction recovery (E_r) can be defined as following equations:

OCTANOL PHASE

$HAuCl_4$ + (CH3CH2CH2CH2CH2CH2CH2CH2)$_3$NCl ⟷ HCl + CH3CH2CH2CH2CH2CH2CH2CH2)$_3$N AuCl$_4$

CH3   CH3

$HAuCl_4$

H$^+$+ Cl$^-$ + CH3CH2CH2CH2CH2CH2CH2CH2)$_3$N AuCl$_4$

CH3

AQUEOUS PHASE

Scheme 1 Overall DLLME for Au(III) determination

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Fig. 1 The effect of the amount of extraction solvents on extracted Au(III) signals. Extraction conditions: sample solution, 10 mL of gold (200 μg L^{-1}); extraction solvent, 1-octanol containing Aliquat 336 (5% *w/v*); HCl concentration (2 mol L^{-1}); disperser solvent 1.5 mL acetone
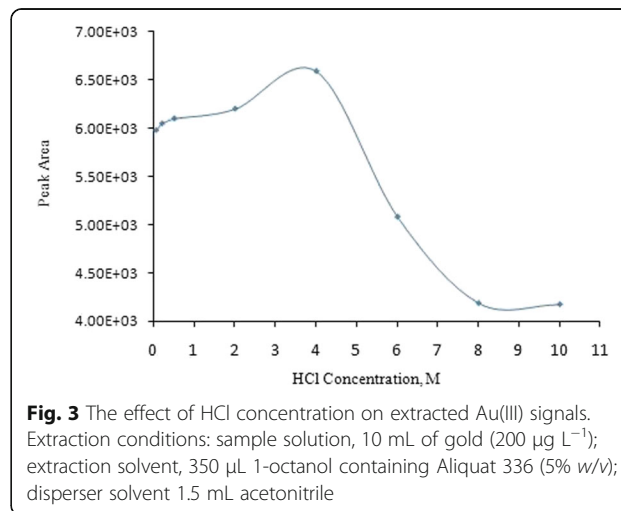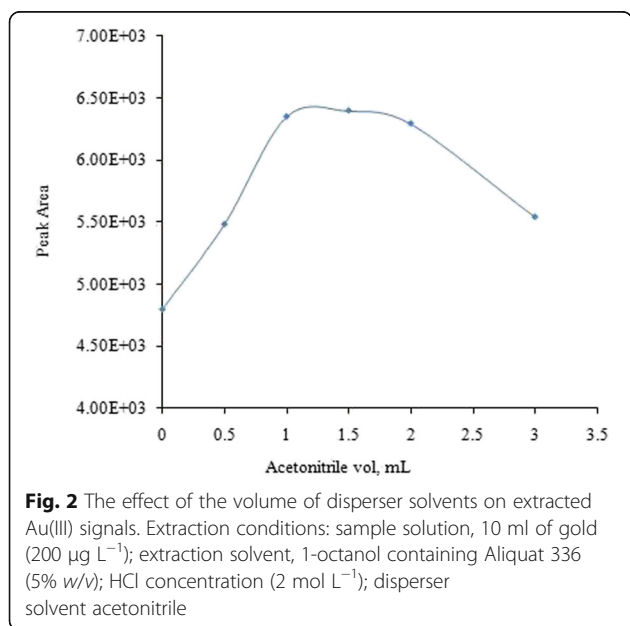
$$E_f = \frac{C_{eq}^e}{C_{ini}^s} \tag{1}$$

$$E_r = \frac{n_{ex}}{n_{ini}} = \frac{C_{eq}^{ex} V_{ex}}{C_{ini}^{sam} V_{sam}} \tag{2}$$

where C_{eq}^o is the final concentration of analyte in the organic phase, C_{ini}^s is the initial analyte concentration in the sample phase, n_{ex} is the moles of the analyte extracted into the extracting phase and n_{ini} is the total moles of the analyte, and V_{ex} and V_{sam} are the final (separated) volume of extracting phase and initial volume of

sample, respectively. As the nature of organic solvent can improve emission signal, enhancement factor can be obtained by division of slope of the calibration curve related to LLE procedure to that of aqueous solution.

$$E_n = \frac{\text{LLE-calibration-slope}}{\text{Aqueous-calibration-slope}} \tag{3}$$

E_f can be also defined as the slope of the calibration curve related to DLLME procedure to that of DLLME procedure (Shamsipour and Ramezani 2008) (Scheme 1).
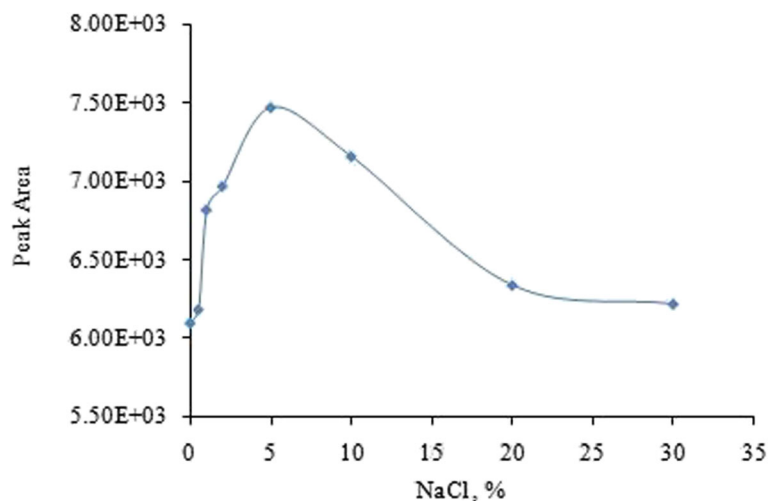

Fig. 2 The effect of the volume of disperser solvents on extracted Au(III) signals. Extraction conditions: sample solution, 10 ml of gold (200 μg L^{-1}); extraction solvent, 1-octanol containing Aliquat 336 (5% *w/v*); HCl concentration (2 mol L^{-1}); disperser solvent acetonitrile

Fig. 3 The effect of HCl concentration on extracted Au(III) signals. Extraction conditions: sample solution, 10 mL of gold (200 μg L^{-1}); extraction solvent, 350 μL 1-octanol containing Aliquat 336 (5% *w/v*); disperser solvent 1.5 mL acetonitrile

Fig. 4 The effect of salt concentration on extracted Au(III) signals. Extraction conditions: sample solution, 10 mL of gold (200 μg L^{-1}); extraction solvent, 350 μL 1-octanol containing Aliquat 336 (5% *w/v*); HCl concentration (2 mol L^{-1}); disperser solvent 1.5 mL acetonitrile

$$E_f = \frac{\text{DLLME-calibration-slope}}{\text{Aqueous-calibration-slope}} \qquad (4)$$

Nature and amount of extraction solvent

Extraction solvent plays a prominent role in a successful extraction procedure (Rezaee et al. 2010). In general, the extraction solvent must be able to extract the analyte well and has low solubility in aqueous medium. High-density extraction solvents, being mostly halogenated, are generally toxic and have high background emission in ICP-OES, accordingly alcohols with lower densities than aqueous solutions and less volatile were chosen in this test. The solvents that were tested in this work are

1-octanol and 1-dodecanol (due to their compatibility with ICP-OES). The results showed that the organic phase after extraction by 1-octanol had higher overall extraction recovery for the target analyte than 1-dodecanol. Therefore, 1-octanol was selected for further studies.

In order to evaluate the effect of extraction solvent volume, different volumes of 1-octanol (i.e., 50 to 600 μL) were examined with the same DLLME procedure. The collected organic phase diluted to 700 μL with 1-octanol and introduced to ICP-OES. The resulting curves of the peak area, obtained by time-scan mode, against the volume of extraction solvent are shown in Fig. 1.
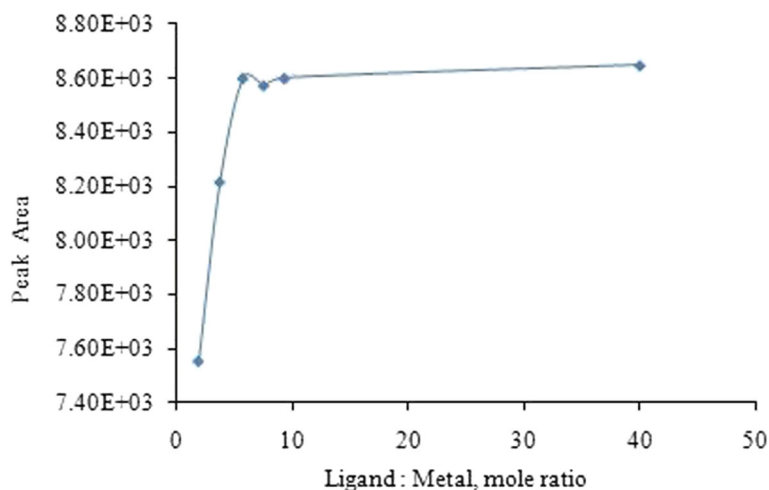

Fig. 5 The effect of the amount of ion-association reagent on extracted Au(III) signals. Extraction conditions: sample solution, 10 mL of gold (200 μg L^{-1}); extraction solvent, 350 μL 1-octanol containing Aliquat 336 (5% *w/v*); HCl concentration (2 mol L^{-1}); disperser solvent 1.5 mL acetonitrile

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The results showed that the peak area (proportional to concentration) of the extracted gold decreased with the increasing volume of 1-octanol in the studied range. However, as expected, the normalized peak area (extraction recovery) increased with the increasing volume of 1-octanol. For trace analysis, high-enrichment factor is more critical than extraction efficiency, so 50 μL of solvent was chosen as the optimized volume for analysis.

Type and amount of disperser solvent

The disperser solvent has to be highly miscible with both water and the extraction solvent. Disperser solvent has an important effect on decreasing the interfacial tension between water and extracting solvent and thus makes the droplet size smaller. Thereby, acetone, ethanol, and acetonitrile which have these properties were tested as disperser solvents in this work. Acetonitrile was chosen as disperser solvent due to its highest emission intensity of extracted phase containing target Au(III).

Since the variation in volume of acetonitrile caused a change in emission intensity of extracted $AuCl_4^-$, it was necessary to optimize the volume of disperser solvent. It was found that at low volume of acetonitrile, the cloudy solution was not completely formed whereas at high acetonitrile volume, there was completely one phase; therefore, it was important to optimize the volume of acetonitrile. The test was done with 10 mL of Au(III) (200 μg L^{-1}) with varying volumes (0.1, 0.5, 1, 2, 4,

Table 1 The effect of foreign ions on pre-concentration and determination of Au(III) (20 μg L^{-1})

Ions	Ion/Au ratio	Extraction recovery (%)
Cr	500	96 ± 6
Co	100	96 ± 6
Cd	500	96 ± 6
Ni	500	96 ± 6
Mn	500	104 ± 6
Pb	500	95 ± 6
Sc	100	96 ± 6
Zn	500	96 ± 6
Ba	100	96 ± 6
Mg	1000	95 ± 6
Al	2000	101 ± 6
Ca	2000	96 ± 6
Na	2000	95 ± 6
Fe	2000	101 ± 6
K	1000	98 ± 6
Pd	500	107 ± 6
Pt	500	107 ± 6
Ir	100	105 ± 6

Table 2 Determination of Au(III) in water samples

Samples	Added (μg L^{-1})	Found value (μg L^{-1})	Recovery (%)
Anguran mine drainage	–	<LOD	–
	10.0	9.9 ± 1.4	99 ± 15
Urumieh Lake	–	<LOD	–
	10.0	10.6 ± 0.7	106 ± 7
Tap water	–	<LOD	–
	60.0	61.6 ± 6.4	102 ± 10

5 mL) of acetonitrile and the results are shown in Fig. 2. As seen, the emission signal of extracted phase increases with the increasing volume of acetonitrile up to 1.5 mL and decreases by increasing the acetonitrile volume.

Effect of HCl concentration

The concentration of HCl is one of the most important parameters that affect the formation of $AuCl_4^-$...Aliquat 336 ion-association compound and its extraction. Thus, the influence of HCl concentration (in the range of 0.1–10 mol L^{-1}) on the extraction of 200 μg L^{-1} of Au(III) from 10 mL aqueous solution by the proposed method was studied. According to the obtained results, the emission signal was increased by increasing the HCl concentration up to 4 mol L^{-1} and start being lessened (Fig. 3). Thereby, 4 mol L^{-1} concentration of HCl for quantitative extraction of Au(III) was selected.

Effect of salt concentration

The influence of the ionic strength on the solution was evaluated by adding different amounts of NaCl up to saturation into the sample solution. The results (Fig. 4) showed that the ionic strength had an obvious effect on emission intensity of extracted $AuCl_4^-$. By increasing the salt amount in solution up to 5%, the extracted Au(III) signals increased, then a decrease in signal was seen.

Amount of ion transfer reagent

The influence of different amount of Aliquat 336 on the extraction efficiency was investigated as the mole ratio of reagent to metal, varying from 1.9 to 40. The results showed that the extracted Au(III) signals sharply increased up to 5.7 mole ratio of the reagent to metal and then remained almost constant. As can be seen from Fig. 5, the optimum amount of the reagent was at the

Table 3 Determination of Au(III) in geochemical reference samples

Sample	Certified (μg g^{-1})	Found (μg g^{-1})	Recovery %
GAU 15	0.30 ± 0.01	0.27	90
GAU 16	1.09 ± 0.04	1.0	91
GAU 17	3.14 ± 0.08	2.9	94

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Table 4 Comparison of different method for determination of gold in aqueous samples

Method	EF	LOD ($\mu g\ L^{-1}$)	RSD (%)	Linear range ($\mu g\ L^{-1}$)	Ref
DLLME-GFAAS	388	0.005	4.2	0.03–0.5	Shamsipour and Ramezani 2008
SPE-FAAS	–	0.8	1.7	50–34000	Sabermahani et al. 2012
CPE-ICP-OES	8.6	0.5	<5	0.5–1000	Tavakoli et al. 2008
SPE-ICP-OES	150	0.32	3.3	–	Zhang et al. 2011
UAE-DLLME-ETAAS	220	0.008	4.2	0.075–0.75	Mohammadi et al. 2010
USAE-SFODMS-FAAS	34.8	0.45	1.68	1.5–400	Tajic and Taher 2011
DLLME-ICP-OES	149	0.09	6	0.3–100	This work

DLLME Dispersive liquid–liquid microextraction, *SPE* Solid-phase extraction, *UAE* Ultrasound-assisted emulsification, *USAE-SFODMS* ultrasound-assisted emulsification of solidified floating organic drops, *CPE* Cloud point extraction

mole ratio of 5.7 and this amount of the reagent solution was used to be optimum in the subsequent experiment.

Effect of foreign ions

The effect of various ions on the efficiency of the method was studied under the optimized conditions. In order to demonstrate the selectivity of the proposed method, the recovery of Au from the sample solution in the presence of various interfering ions which are reported to be usually present in different gold real sample (Hassani Pak 2002) was investigated according to the recommended procedure. A relative error of 5% was considered tolerable. The summarized results in Table 1 showed that these metal ions did not show any interfering effect at their studied levels for the determination of gold in various samples.

Calibration graph and real sample

The analytical characteristics of the proposed method were constructed under optimized conditions. These quantitative parameters were calculated using the values of the signals for analytical curve. The equation of linear calibration graph after pre-concentration procedure was $y = 43.5x - 10.8$ with a regression coefficient better than 0.993 where y is the emission signal of the considered element and gold concentration (x) is expressed in $\mu g\ L^{-1}$. The limit of detection and quantification for gold, calculated according to $3S/m$ and $10S/m$ criteria (being S the standard deviation of 8 consecutive blanks and m the slope of calibration graph), were 0.09 and 0.32 $\mu g\ L^{-1}$, respectively. The precision of the method was found to be 6% as the relative standard deviation of five replicates and recoveries of 10 $\mu g\ L^{-1}$ Au(III) from 10 mL aqueous solution. The enrichment factor for the proposed method defined as the slope of calibration curves with and without pre-concentration was found to be 150. The suggested procedure was applied to determine Au(III) in different water samples. When no aqueous standard reference materials with a certified content of target analyte are available, an add–found method can be considered as an alternative for validation studies (Yamini et al. 2012). Tap, lake, and mine water samples were collected in acid-leached polyethylene bottles, and the results are summarized in Table 2. The accuracy of the method was further verified by the determination of the amount of gold ions in some geological reference samples (GAU 15–17) (Table 3). As it is obvious, the extraction efficiency was excellent and showed no serious matrix effects.

Comparison with other methodologies

As shown in Table 4, the main analytical characteristics of the present method for Au(III) pre-concentration/determination are compared with those of some of the previously reported methods in the literature. As can be seen, the proposed procedure shows good detection limit, wide linear dynamic range, and good enrichment factor comparable with several reported methods.

Conclusions

Au(III) can be selectively extracted from a sample solution in HCl (4 mol L^{-1}) media at the presence of other elements such as Cr, Co, Pt, and Pd. The combined DLLME method with ICP-OES can readily determine Au(III) at $\mu g\ L^{-1}$ level using only 10 mL of sample solution without interference by the matrices. In this method, using toxic-chlorinated solvents that are commonly used as extraction solvents is avoided. As the solvent and circumstances are compatible with ICP-OES, there is no need to evaporate solvent for elemental analysis. This methodology is a simple, fast, green, and low cost which can be used with ICP-OES technique so could be of great interest for Au(III) determination in routine analytical laboratories.

Authors' contributions
All authors read and approved the final manuscript.

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Competing interests

The authors declare that they have no competing interests.

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