

# Development of cloud point extraction for simultaneous extraction and determination of gold and palladium using ICP-OES

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Received 17 April 2007; received in revised form 13 July 2007; accepted 15 July 2007

Available online 19 July 2007

## Abstract

Cloud point method was applied for the simultaneous extraction and preconcentration of trace amounts of gold and palladium. The extraction of analytes was performed in the presence of 1,8-diamino-4,5-dihydroxy anthraquinone as chelating agent and Triton X-114 as a non-ionic surfactant. After phase separation, the surfactant-rich phase was diluted with concentrated HNO<sub>3</sub> (65%, w/w) and the analytes concentrations were determined by inductively coupled plasma-optical emission spectrometry (ICP-OES). The variables affecting the complexation and extraction conditions were optimized and under the optimum conditions (i.e. pH 6.5,  $2.2 \times 10^{-4}$  mol l<sup>-1</sup> chelating agent, 0.15% (w/v) of Triton X-114, equilibration temperature 55 °C, centrifuge at 3500 rpm), quantitative extraction of Au(III) and Pd(II) from 100 ml of the aqueous solution was performed. The calibration curves were linear in the range of 0.5–1000 μg l<sup>-1</sup> with detection limits of 0.5 and 0.3 μg l<sup>-1</sup> and the enrichment factors were 8.6 and 20.2 for Au and Pd, respectively. Also the precision (%RSD) for eight replicate determinations of the analytes was better than 5%. Finally, the proposed method was successfully applied for the determination of Au and Pd in mine stones and standard reference materials (SRM).

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**Keywords:** Cloud point extraction; Palladium; Gold; 1,8-Diamino-4,5-dihydroxy anthraquinone

## 1. Introduction

Palladium (Pd) is one of the most widely used of the six platinum group metals (PGM). Pd is especially valued for its catalytic functions, conductivity and resistance to corrosion. It is essential in key manufacturing processes in the automobile, chemical petroleum refining, pharmaceutical and electronics industries. Gold (Au) was the first metal known to man [1].

Pd and Au are valuable mineral elements that occur together in nature. Determination of their trace amounts is of great importance. Measurement of very low concentrations of Au and Pd usually requires separation and preconcentration steps [2–5]. In recent years, the development of analytical methods for the extraction and determination of Pd contents in various matri-

ces have attracted considerable interest. Solid-phase extraction in conjunction with different determination methods [6–9], ion-imprinted polymer extraction with spectrophotometric detection [10], HPLC and on-line SPE-HPLC [11–12], stopped flow injection liquid–liquid extraction with spectrophotometric detection [13] and FIA-FAAS system including on-line SPE [14] have been reported for extraction and determination of Pd.

On the other hand, HPLC [12], atomic absorption spectrometry (AAS) [15,16], ICP-MS after cloud point extraction [17] and solid-phase extraction-AAS [18] have been employed for determination of Au in various matrices.

The applications of micellar systems or other organized molecular assemblies have been recognized many years ago, and exploited in different fields of analytical chemistry in the last decades. Watanabe et al. [19,20] suggested for the first time in 1978 an unconventional liquid–liquid extraction method known as cloud point extraction (CPE) to extract metallic ions from aqueous samples. CPE is based on application of concentrated

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aqueous solution of some non-ionic and zwitterionic surfactants that form homogeneous solution in definite conditions. By changing experimental conditions such as temperature and pressure or in the presence of additives, these solutions become cloudy due to the diminished solubility of the surfactant in water. This phenomenon is denominated as cloud point. In the cloud point extraction method, any component (originally present in the solution that interacts with the micellar aggregates), can be extracted into the small volume of the surfactant-rich phase. The small volume of the surfactant-rich phase obtained in this method (generally between 100 and 400  $\mu\text{l}$ ) permits the design of extraction schemes that are simple, safe, cheap and efficient in comparison with the liquid–liquid extraction (LLE) methods. CPE has been developed in the recent two decades and wide applications for the extraction of metal species and organic molecules have been found [21–28].

In this work, cloud point preconcentration method was developed and optimized for the determination and extraction of Au and Pd in the aqueous samples. Au and Pd were changed into their chelates in the presence of 1,8-diamino-4,5-dihydroxy anthraquinone followed by extraction into octyl phenoxy polyethoxy ethanol (Triton X-114) as a non-ionic surfactant. Finally, simultaneous determination of these elements was performed by ICP-OES and the proposed method was successfully applied to the real samples.

## 2. Experimental

### 2.1. Reagents and materials

All chemicals used were of analytical reagent grade. Pd(II) stock solution ( $1000\text{ mg l}^{-1}$ ) was prepared by dissolution of proper amount of  $\text{PdCl}_2$  (Merck, Darmstadt, Germany) in 3:1,  $\text{HCl}/\text{HNO}_3$  (v/v) according to the standard methods and then diluted with double distilled water [29]. The stock solution of Au(III) ( $1000\text{ mg l}^{-1}$ ) was purchased from Merck. These standard solutions were diluted with distilled water to prepare mixed stock solution of the analytes with  $100\text{ mg l}^{-1}$  and  $10\text{ mg l}^{-1}$  concentration.

All the working solutions were freshly prepared by diluting the mixed stock solution (containing both of the metal ions) with buffer solution to the required concentration after addition of ligand and surfactant. Reagent grade 1,8-diamino-4,5-dihydroxy anthraquinone was a gift from Iran Color Research Center (Tehran, Iran) used as chelating agent (Fig. 1). Standard solution of ligand ( $10^{-3}\text{ mol l}^{-1}$ ) was prepared by dissolving proper amount of ligand in extra pure acetone (Merck).

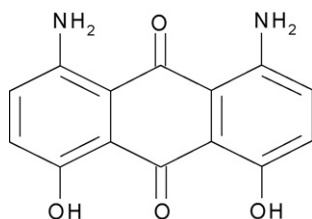


Fig. 1. Chemical structure of 1,8-diamino-4,5-dihydroxy anthraquinone.

The non-ionic surfactant; Triton X-114, Fluka (Chemie AG, Switzerland) was used without further purification. A 1.25 g of Triton X-114 was dissolved in 50 ml of distilled water to give a 2.5% (w/v) of surfactant solution. The buffer solution (pH 6.5) was prepared by dissolving appropriate amounts of sodium acetate ( $0.10\text{ mol l}^{-1}$ ) and addition of nitric acid (Merck) and sodium hydroxide (Merck) solutions to reach the required pH.

The vessels used for trace analysis were kept in 10% (w/v) nitric acid at least for 24 h and subsequently washed four times with double distilled water.

### 2.2. Apparatus

Simultaneous inductively coupled plasma-optical emission spectrometry (ICP-OES Varian Vista-Pro, Australia) coupled to a V-groove nebulizer and equipped with a charge coupled device detector (CCD) was used for simultaneous measurements of Pd and Au in the surfactant-rich phase. The observation mode was radial-viewing. The argon gas with the purity of 99.999% for ICP-OES was purchased from Roham Gas Company (Tehran, Iran). Au and Pd determinations in the optimization section of CPE parameters were carried out on a Shimadzu AA-680 atomic absorptions spectrometer (AAS) with Au and Pd hollow cathode lamps at 244.2 nm and 242.8 nm, respectively, using an air–acetylene flame. A thermostated water-bath GFL (model D 3006 Burg Wedel) was employed for adjusting the temperature of the solutions in CPE experiments and a Mistral 3000i centrifuge (England) was utilized to accelerate the phase separation process.

### 2.3. Procedure

For CPE experiments, aliquots of solution ( $V = 10\text{ ml}$  and pH 6.5) containing the mixture of  $5\text{ mg l}^{-1}$  of the analytes, ligand ( $2.2 \times 10^{-4}\text{ mol l}^{-1}$ ) and 0.15% (w/v) Triton X-114 were kept in the thermostated water-bath at  $55^\circ\text{C}$  (the temperature above the cloud point temperature) for 15 min. Since the surfactant is denser than water, the surfactant-rich phase typically settles through the aqueous phase. In order to accelerate the phase separation, the turbid solutions were centrifuged at 3500 rpm for 8 min, and then cooled in an ice-bath for 10 min to increase the viscosity of the surfactant-rich phase. The aqueous phase was carefully removed with a pipette. The surfactant-rich phase (nearly  $250\text{ }\mu\text{l}$ ) was diluted to 5 ml with  $\text{HNO}_3$  (65%, w/w) to reduce its viscosity and increase the sample volume for the ICP-OES measurement.

Finally, the samples were introduced into the flame or plasma with peristaltic pump. Emission intensities in the ICP-OES signals were measured at 267.594 and 340.458 nm for Au and Pd, respectively. It is worthy to note that at selected wavelength, the detection limits of direct ICP-OES for Au and Pd were 55 and  $70\text{ }\mu\text{g l}^{-1}$ , respectively.

All the optimization experiments were done using Falcon tubes with 10 ml volume and AAS was applied for determination of the elements concentrations. In the case of calibration graphs and real samples, for increasing the concentration factor,

Falcon tubes with 100 ml volumes were applied and determination of the elements concentration was performed using ICP-OES.

### 3. Results and discussion

#### 3.1. Method development

Before analysis of the standard and real samples by ICP-OES, proper conditions of the instrument should be obtained. Thus, different parameters influencing the intensity of signals in ICP-OES such as radio frequency (rf), generator power, nebulizer pressure, viewing height of plasma, auxiliary gas flow rates and peristaltic pump rate were optimized. Then, to ensure that maximum extraction efficiency was attained, the parameters affecting CPE efficiency including surfactant and chelating agent concentration, equilibrium time and temperature, pH of solution and centrifuge time were optimized using the univariate optimization approach. The procedural parameters included in the optimization are given in the following section in order to gauge the importance of each. The optimized conditions of ICP-OES were tabulated in Table 1.

#### 3.2. Influence of reagent concentration

In CPE, the nature of the chelating agent and its concentration are most important factors. CPE can be used for preconcentration of metal ions after the formation of sparingly water-soluble complexes between the ions and the ligand. CPE efficiency depends on the hydrophobicity of the ligand and the formed complex, the apparent equilibrium constants in the micellar medium, the kinetics of the complex formation and the transference between the phases [30].

Fig. 2 shows the effect of ligand concentration on the CPE of Au and Pd. In the present study the effect of the ligand's concentration was tested in the range of  $0\text{--}5.1 \times 10^{-4} \text{ mol l}^{-1}$ . Maximum extraction efficiency was obtained at the concentration of  $2.2 \times 10^{-4} \text{ mol l}^{-1}$  of the ligand. Thus, concentration of  $2.2 \times 10^{-4} \text{ mol l}^{-1}$  was chosen for further extractions. Using an excess amount of the ligand was found to decrease the extraction efficiency, because for utilizing higher concentrations of the chelate, more acetone as the ligand's solvent was used. Accordingly, higher volumes of acetone can prevent the micelle formation and reduce the extraction efficiency.

Table 1  
The optimized conditions for ICP-OES for determination of Pd and Au ions

RF generator power (kW)	1.65	Au wavelength (nm)	267.594
Frequency of RF generator (MHz)	40	Pd wavelength (nm)	340.458
Plasma gas flow rate ( $\text{l min}^{-1}$ )	12.0	Viewing height (mm)	9
Auxiliary gas flow rate ( $\text{l min}^{-1}$ )	0.75	Pump rate (rpm)	15
Nebulizer pressure (kPa)	240		

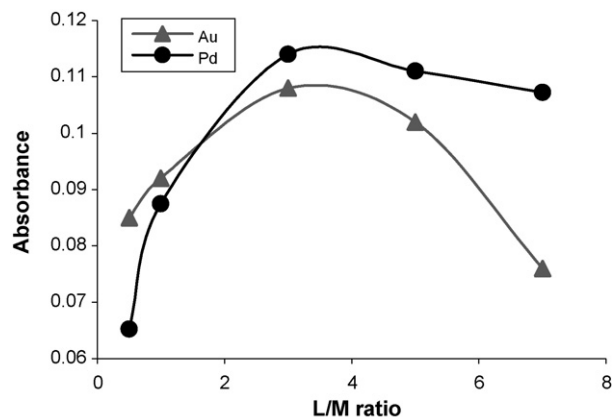


Fig. 2. Effect of reagent concentration on the extraction of Au and Pd complexes. Extraction conditions:  $5 \text{ mg l}^{-1}$  of Au and Pd, 0.15% (w/v) Triton X-114, equilibration temperature;  $55^\circ\text{C}$  (for 15 min) and centrifuge time; 8 min.

#### 3.3. Effect of Triton X-114 concentration

A successful CPE should maximize the extraction efficiency and minimize the phase volume ratio in order to increase the concentrating factor. The effect of variation of the concentration of Triton X-114 in the range of 0.0–0.5% (w/v) on extraction efficiency was examined. The differences observed in the signals at various surfactant concentrations are shown in Fig. 3. At 0.15% (w/v) of Triton X-114, nearly perfect extraction of both analytes occurred. At lower concentrations of the surfactant the extraction efficiency was low probably due to inadequacy of the assemblies to entrap the hydrophobic complex quantitatively. At concentrations above 0.15% (w/v), the signals intensity decreases probably due to increment in the viscosity of the surfactant phase. To achieve maximum preconcentration factor, Triton X-114 concentration was chosen as 0.15% (w/v).

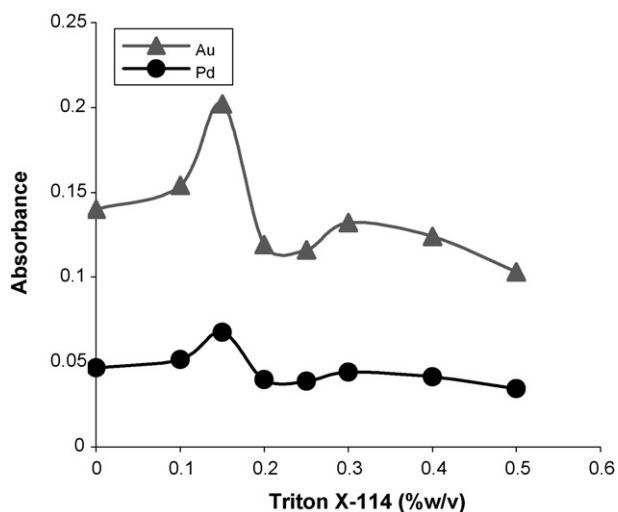


Fig. 3. Effect of Triton X-114 on the extraction of Au and Pd complexes. Extraction conditions:  $5 \text{ mg l}^{-1}$  of Au and Pd,  $2.2 \times 10^{-4} \text{ mol l}^{-1}$  of 1,8-diamino-4,5-dihydroxy anthraquinone, equilibration temperature;  $55^\circ\text{C}$  (for 15 min) and centrifuge time; 8 min.

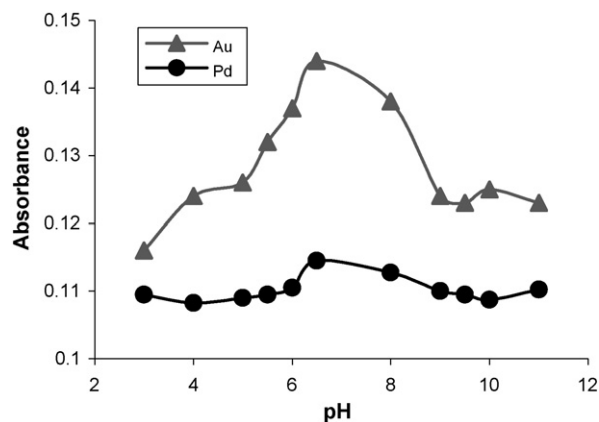


Fig. 4. Effect of pH on the extraction of Au and Pd complexes. Extraction conditions:  $5 \text{ mg l}^{-1}$  of Au and Pd,  $2.2 \times 10^{-4} \text{ mol l}^{-1}$  of 1,8-diamino-4,5-dihydroxy anthraquinone, 0.15% (w/v) Triton X-114, equilibration temperature;  $55^\circ\text{C}$  (for 15 min) and centrifuge time; 8 min.

### 3.4. Effect of pH and ionic strength

Separation of metal ions by CPE method involves prior formation of a complex with sufficient hydrophobicity which could be extracted into the small volume of surfactant-rich phase. Extraction yield depends on the pH at which complex formation is carried out. Fig. 4 shows the effect of pH on the extraction of Au and Pd complexes. The effect of pH upon the complex formation of the analytes was studied in the range of 3–11. For both of the analytes, the maximum absorbance was observed between 6 and 8, hence, pH 6.5 was chosen for further extractions.

The effect of sodium chloride concentration on the extraction efficiency was examined. It was found that addition of NaCl to the solution in the range of  $0.0\text{--}1.0 \text{ mol l}^{-1}$  had no significant effect on the extraction efficiency. This is in agreement with the literature results, demonstrating that an increase in ionic strength in micellar system does not seriously alter the extraction efficiency of the analytes [8].

### 3.5. Influence of equilibrium temperature and time

The equilibration temperature and the incubation time were the next parameters considered. It was desirable to employ the shortest incubation time and the lowest possible equilibration temperature, which compromise completion of reaction and efficient separation of phases.

For Triton X-114, an increase in the cloud point temperature leads to a slight decrease in the volumes of the surfactant-rich phase. This can be interpreted in terms of the fact that as temperature increases, hydrogen bonds are disrupted and dehydration occurs. With the increasing of temperature, the amount of water in the surfactant-rich phase reduces and, hence, the volume of that phase decreases [31].

The cloud point temperature of Triton X-114 is  $25^\circ\text{C}$  [32]. Some studies have indicated that in order to obtain a more favorable preconcentration factor, CPE should be carried out at the temperatures sufficiently higher than the cloud point temperature. In this study, the effect of equilibration temperature

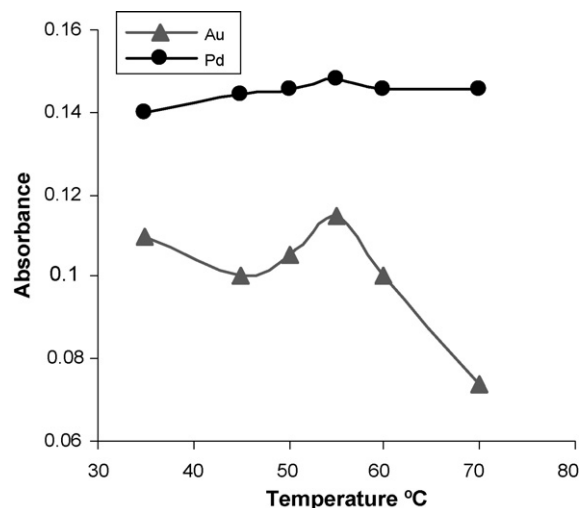


Fig. 5. Effect of equilibration temperature on the extraction of Au and Pd complexes. Extraction conditions:  $5 \text{ mg l}^{-1}$  of Au and Pd,  $2.2 \times 10^{-4} \text{ mol l}^{-1}$  of 1,8-diamino-4,5-dihydroxy anthraquinone, 0.15% (w/v) Triton X-114, pH 6.5 (acetic acid/acetate buffer) and centrifuge time; 8 min.

was investigated in the range of  $35\text{--}70^\circ\text{C}$  (Fig. 5). The optimal temperature was found to be  $55^\circ\text{C}$  for the CPE of both analytes. Further investigation of the effect of incubation time showed that the maximum extraction efficiency was observed at 0–20 min. Thus, very short incubation times were applied in further experiments.

### 3.6. Effect of centrifugation time

Centrifugation times at 3500 rpm were examined in the range of 2–15 min. Eight minutes was selected as optimum centrifugation time, because complete separation occurred at this time and no appreciable improvements were observed for longer times. However, the centrifugation time did not have considerable effect on the analytical characteristics of the CPE method.

### 3.7. Influence of the surfactant-rich phase viscosity

The final surfactant-rich phase volume sedimented from 10 ml of the cloudy solution was determined 0.25 ml. Since the surfactant-rich phase obtained after separation of the phases was very viscous; it was diluted with concentrated  $\text{HNO}_3$  in order to facilitate its introduction into the nebulizer of the AAS or ICP-OES instruments. Several organic solvents instead of  $\text{HNO}_3$  were tested. In the presence of organic solvent absorbance signals of Au and Pd were diminished. Thus, the surfactant-rich phase was diluted to 5 ml using  $\text{HNO}_3$  (65%, w/w) in the subsequent experiments.

### 3.8. Figures of merit

Calibration graphs were obtained using 100 ml of the standard solutions of Au and Pd ions buffered at pH 6.5 and containing 0.15% (w/v) Triton X-114 at optimal conditions. The obtained results showed that the calibration graphs were linear in the concentration range of  $0.5\text{--}1000 \mu\text{g l}^{-1}$  for Pd

Table 2  
Analytical characteristics of CPE method

Parameter	Au	Pd
Wavelength (nm)	267.594	340.458
Limit of detection ( $\mu\text{g l}^{-1}$ )	0.5	0.3
%RSD ( $n=8$ , $C=5\text{ mg l}^{-1}$ )	4.9	3.8
Regression equation	$I=5.64C$ ( $\mu\text{g l}^{-1}$ )+66.75	$I=13.89C$ ( $\mu\text{g l}^{-1}$ ) – 92.52
Correlation coefficient	0.9926	0.9974
Enrichment factor	8.6	20.2

and 1.5–1000  $\mu\text{g l}^{-1}$  for Au. Analytical characteristics of the proposed method are presented in Table 2. The standard deviations (RSDs) resulted from the analysis of eight replicates of the 10 ml solution containing 5  $\text{mg l}^{-1}$  Au and Pd were 4.9% and 3.8%, respectively. The detection limits (calculated as the concentration equivalent to three times of the standard deviation of the blank divided into the slope of the calibration graph) were 0.5 and 0.3  $\mu\text{g l}^{-1}$  for Au and Pd, respectively. The enrichment factor was calculated as the ratio of slope of the calibration curve obtained from the preconcentrated samples to that obtained without preconcentration. Accordingly, enrichment factors of 8.6 and 20.2 were obtained for Au and Pd, respectively.

### 3.9. Interferences

In the view of the high selectivity provided by ICP-OES, the only interferences studied were those related to the preconcentration step. Several metal ions that might react with anthraquinone were examined for their effect on the recoveries of Au and Pd. To perform this study, the amounts of Au and Pd was set at 5  $\text{mg l}^{-1}$ ; the concentrations of Triton X-114 and anthraquinone were set at 0.15% (w/v) and at  $2.2 \times 10^{-4}\text{ mol l}^{-1}$ , respectively.

The results are shown in Table 3. One can see that presence of alkaline, alkaline earth and transition metal ions did not have any adverse effects on the extraction efficiency of Au and Pd ions. It is worthy to note that interferences by foreign cations affect the reagent's concentration; therefore, any reagent loss could be avoided by increasing its concentration.

### 3.10. Determination of Au and Pd in real samples

In order to test the reliability of the proposed CPE method for extraction and determination of Au and Pd in the real samples, several mine stones were applied. For this purpose, each mine stone was grinded and proper amount of it was weighted in the range of 2–4 g, and digested in 3:1 HCl/HNO<sub>3</sub> by refluxing the mixture for 15 h. The solution of each sample was centrifuged and filtered. The filtered solution was diluted with HNO<sub>3</sub> (65%, w/w) up to 20 ml. Finally, 5.0 ml of this solution was poured into Falcon tubes and after addition of sodium acetate and adjustment of pH, the volume of solution was adjusted to 10 ml. The solution was then extracted using the proposed method at the optimal conditions. The results are

Table 3  
Effects of the foreign ions on the recovery of 0.5  $\text{mg l}^{-1}$  of Au and Pd from the aqueous solutions

Ions	Concentration ( $\text{mg l}^{-1}$ )	Ion/Au or Pd ratio (w/w)	Recovery (%)	
			Au	Pd
Li <sup>+</sup> , Na <sup>+</sup> , K <sup>+</sup> (mixture)	5000 (each ion)	1000	102.0	103.0
Ca <sup>2+</sup>	5000	1000	66.3	46.00
	2000	500	98.3	90.00
Co <sup>2+</sup>	2500	500	88.4	96.90
	1000	200	104.0	98.00
Mg <sup>2+</sup>	2000	400	100.5	102.8
Sr <sup>2+</sup>	5000	1000	100.7	104.0
Ba <sup>2+</sup>	5000	5000	108.0	101.0
Al <sup>3+</sup>	5000	1000	98.0	36.0
	2500	500	98.0	48.0
	1000	200	102.0	95.0
Cd <sup>2+</sup>	5000	1000	102.0	104.0
	2500	500	88.7	87.8
As(III)	1000	200	106.0	92.0
	5000	1000	93.0	80.6
Mn <sup>2+</sup>	2500	500	103.0	89.4
	5000	1000	107.0	104.0
Hg <sup>2+</sup>	5000	100	107.0	104.0
	5000	1000	90.0	69.1
Ni <sup>2+</sup>	2500	500	102.0	79.8
	1000	200	107.0	104.0
	5000	1000	94.9	97.0
Zn <sup>2+</sup>	1000	1000	94.9	101.9
Pb <sup>2+</sup>	5000	1000	105.3	104.0
Fe <sup>3+</sup>	2500	500	81.5	99.7
	1000	200	103.8	104.0
Fe <sup>2+</sup>	1000	200	103.1	102.7
	5000	1000	91.5	104.0
Mo <sup>2+</sup>	2500	500	100.7	104.0
	5000	1000	107.0	105.0
Pt(II)	500	100	107.0	105.0

shown in Table 4. Good agreement between the table results and known values indicates the successful applicability of the present method for simultaneous determination of Au and Pd in the real samples.

Table 4  
Determination of Au and Pd in mine stones

Real samples	Certified ( $\text{mg l}^{-1}$ ) <sup>a</sup>		Found ( $\text{mg l}^{-1}$ )		Recovery (%)	
	Au	Pd	Au	Pd	Au	Pd
1	7.0	–	7.3	–	104.2	–
2	6.4	–	6.3	–	99.6	–
3	1.1	–	1.0	–	91.6	–
4	0.6	–	0.7	–	105.2	–
5	13.4	–	13.1	–	97.8	–
6	14.8	–	16.5	–	111.5	–
7	–	1.7	–	1.5	–	90.0
8	–	4	–	4.3	–	108.0

<sup>a</sup> Certified concentration of the elements were reported by Geological Survey of Iran (Tehran, Iran).



#### 4. Conclusions

Some advantages of CPE in comparison with similar extraction systems using organic solvents are: experimental convenience, low cost, easy and safe methodology for preconcentration and separation of trace elements in aqueous solutions. Triton X-114 was chosen for the CPE due to its excellent physicochemical characteristics; low cloud point temperature, high density of the surfactant-rich phase, which facilitates phase separation easily by centrifugation, commercial availability and relatively low price and toxicity. The obtained results showed that anthraquinone is an efficient ligand for cloud point extraction of Au and Pd.

The proposed CPE method is suitable for preconcentration of Au and Pd cations as a prior step to their determination by ICP-OES. Simple accessibility, formation of stable complexes, selectivity and enhanced analytical sensitivity due to the fact that the complex can be easily extracted from the bulk aqueous solution into much smaller volumes of the surfactant-rich phase are the major advantages of the CPE. In this method, a very low limit of detections and good precisions (low %RSDs) were obtained for Au and Pd. The method was also verified with real samples and satisfactory results were obtained for the simultaneous determination of Au and Pd in very complex matrices such as stone samples.

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