Cloud point extraction of palladium in water samples and alloy mixtures using new synthesized reagent with flame atomic absorption spectrometry (FAAS)

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Abstract

The present paper outlines novel, simple and sensitive method for the determination of palladium by flame atomic absorption spectrometry (FAAS) after separation and preconcentration by cloud point extraction (CPE). The cloud point methodology was successfully applied for palladium determination by using new reagent 4-(2-naphthalenyl)thiozol-2yl azo chromotropic acid (NTACA) and hydrophobic ligand Triton X-114 as chelating agent and nonionic surfactant respectively in the water samples and alloys. The following parameters such as pH, concentration of the reagent and Triton X-114, equilibrating temperature and centrifuging time were evaluated and optimized to enhance the sensitivity and extraction efficiency of the proposed method. The preconcentration factor was found to be (50-fold) for 250 ml of water sample. Under optimum condition the detection limit was found as 0.067 ng ml^{-1} for palladium in various environmental matrices. The present method was applied for the determination of palladium in various water samples, alloys and the result shows good agreement with reported method and the recoveries are in the range of 96.7–99.4%.

1. Introduction

Palladium has extensive use in alloys, catalysts and in low voltage electrical contacts. It is an efficient catalyst that is widely used for hydrogenation and dehydrogenation reactions. The palladium content of earth crust is 0.01–0.02 µg ml^{-1} owing to corrosion resistance nature and it exists in various natural minerals, soil and rocks. Palladium and its alloys have wide range of application in both in chemical industries and instrument making. It is used in jewelry, dentistry applications, fine instruments, such as watches and some surgical tools for the purification of hydrogen gas [1]. The carcinogenicity of palladium compounds in rates and mice and their toxicity to mammals, fish and higher plants are causes for environmental concern. Therefore, these compounds usually considered as environmental pollutants. The direct determination of palladium in various environmental samples with different instrumental methods is not possible to decrease the concentration levels of trace amounts in different environmental samples. The Azo dyes with the heterocyclic diazo-component form colored complexes with many metal ions in solution [2–6]. Several analytical techniques have reported for the determination of trace elements in natural water like ICP-AES, ICP-MS, ETAAS, GFAAS, NAA, CE which are very expensive and in addition to that direct determination of trace metal ions by following methods is not sufficiently sensitive. So many spectrophotometric methods has been developed for the determination of palladium [7–15]. To overcome the above drawbacks it requires previously separation and preconcentration technique which is subsequent determination with FAAS.

Cloud point extraction is an alternative preconcentration technique that reduces the consumption and exposures to a solvent and extraction time and disposal time aqueous

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solution of nonionic surfactants may form two phases in a narrow temperature range called cloud point. The micellar solution separates in to a surfactant concentration (CMC). This phenomenon is in particularly observed for poly oxy ethylene surfactant and can be attributed to the ethyleneoxide segments in the micelle when they are hydrated and that attract each other as the temperature increase due to de hydration. The cloud point phenomenon is reversible and when the temperature is falls bellow the CPT a single phase appear again. Several Preconcentration methods and separation techniques such as liquid-liquid extraction [16], co-precipitation [17], ion-exchange [18,19], sorption on the various adsorbents such as activated carbon [20], silica [21,22], polymeric resin [23–26], activated columns [27], Amberlite XAD resins [28] and other sorbents [29–31], cloud point extraction is a facile, rapid and versatile technique employed for preconcentration and analysis of pesticides, polychlorides and phenols [32,33]. The analytical application of the cloud point phenomenon extend the extraction of toxic organic compound, medical drugs, vitamins and oils to the extraction of metal chelates, with several detection techniques. 8-Hydroxyquinoline was used as a complexing agent in cloud point extraction coupled with ICP-MS [34], ICP-AES [35], AAS [36–38] and FAAS [39] in natural water samples.

In the present study, a novel reagent 4-(2-naphthalenyl)-thiozol-2yl azo chromotropic acid (NTACA) was synthesized for the cloud point extraction and preconcentration of palladium from various water samples and alloys. The method was based on the complexation of palladium with 4-(2-naphthalenyl)thiozol-2yl azo chromotropic acid (NTACA) in presence of Triton X-114 (non-ionic surfactant) at pH 6 ± 0.2 using with suitable buffer (phosphate buffer). Optimum experimental conditions were investigated with respect to a standard solution of the same matrix, in order to examine the possibility to obtaining the maximum extraction efficiency with minor sample treatment and minimal experimental conditions. This is an alternative method to the solid phase extraction and column techniques for the analysis of metal ions in various samples of environmental importance.

2. Experimental

2.1. Instrumentation

A Perkin-Elmer Model 280 atomic absorption spectrometry (AAS) with acetylene flame and hallow cathode lamps was used for the determination of palladium. All instrumental settings and operating conditions were tabulated in Table 1. A HITACHI U 2001 Spectrophotometer with 1.0 cm matched quartz cells was used for all absorbance measurements. A pH meter, Elico Li-129 model glass-calomel combined electrode was employed for measuring pH values.

2.2. Reagents and solutions

All reagents used were of analytical reagent grade. Doubly distilled water and high purity reagents were used for all preparations of the standard and sample solutions. All chemicals were

Table 1
Recommended procedure conditions

Analytical wavelength (nm)	350.4
Lamp current (mV)	5
Air flow-rate ($l\,h^{-1}$)	480
Acetylene flow-rate ($l\,h^{-1}$)	120
Coolent water ($l\,min^{-1}$)	1.5
Recorder grade (mV)	20
Trap stub position	–
Blow the light path (mm)	5
Above the burner (mm)	6

purchased from Merck chemicals, Mumbai, India. Standard stock solution of palladium(II) chloride (0.01 mol l^{-1}) was prepared by dissolving 0.1779 g of PdCl$_2$ 100 ml of water acidified with 0.5 ml of concentrated hydrochloric acid. The resulting solution was standardized gravimetrically using the dimethylglyoxime method [48]. Working solutions were obtained by suitable dilution of the stock solution with deionized-distilled water. The non-ionic surfactant Triton X-114 (Merck chemicals, Mumbai, India) was used without further purification. 0.01% 4-(2-naphthalenyl)thiozol-2yl azo chromotropic acid (NTACA) was prepared by dissolving 0.01 g in 10 ml of ethanol and made up to the mark with 100 ml of doubly distilled water in 100 ml standard flask.

Buffer solution pH 6 ± 0.2 was prepared by adding concentrated acetic acid (7.0 ml) to 250 ml distilled water in a 500 ml flask. Then monosodium dihydrogen phosphate monohydrate (20 g) was added and the flask shaken until dissolution was completed. The solution was then diluted to 500 ml. It was stored in a clean metal free polyethylene bottle (Scheme 1).

2.3. Synthesis of 4-(2-naphthalenyl)thiozol-2yl azo chromotropic acid (NTACA)

2-Amino-4-(2-naphthalenyl)thiazole was prepared according to reported method [48]. The newly synthesized reagent was prepared by diazotization. For diazotization 2.0 g of 2-amino-4-(2-naphthalenyl)thiazole was dissolved in 50 ml of aqueous ethanol and 2% sodium nitrite of 10 ml was added drop wise and stirred at 0–5 °C for 1 h. For coupling, 7.0 g of chromotropic acid was added to 50 ml of ethanol and the mixture was cooled to 0–5 °C. This solution was added drop wise to the above diazotized solution with vigorous stirring. The system was allowed to stand overnight in refrigerator at 0–5 °C. The resulting black precipitate was filtered and purified by recrystallization with ethanol. The yield was 92%. From the elemental analysis the composition of C$_{36}$ H$_{23}$ N$_6$ O$_8$ S$_4$ is found (calculated): C = 54.33 (54.28)%, H = 2.91 (2.85)%, O = 16.10 (16.05)%, N = 10.56 (10.50)%, S = 16.10 (16.03)%.

3. Procedure

3.1. General procedure

An aliquots of 100 ml of the cold standard or sample solution containing the analysts 0.1% (w/v) is taken in to a polypropy-
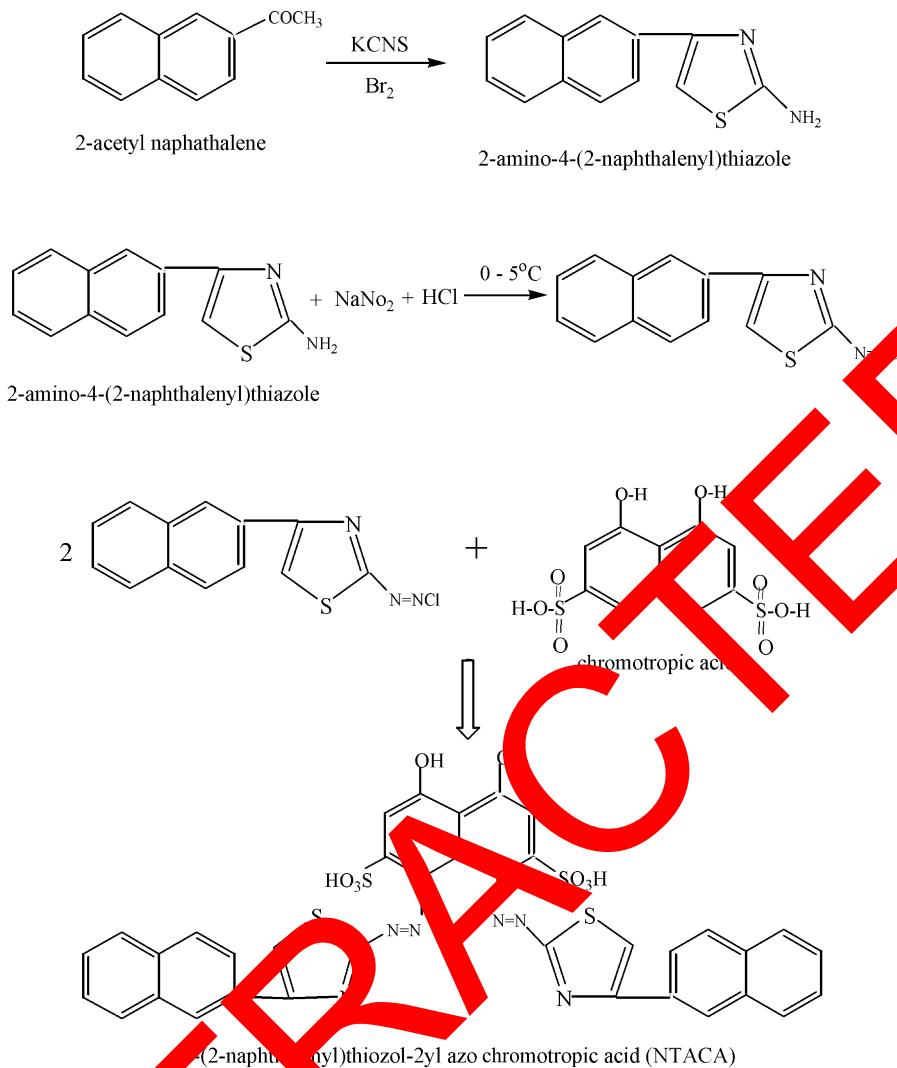
Scheme 1. Metal chelation of palladium(II) with NTACA.

lene tubes, Triton X-114 (0.14%) and 0.004 M reagent were added and the pH was adjusted to 6.0 ± 0.2 with convenient buffer (phosphate buffer). The total system was placed for 10 min in a thermostatic bath at 50 °C. The separation of the two phases was achieved by centrifugations at 3500 rpm. The phases were cooled in an ice bath in order to increase the viscosity of the surfactant-rich phase. The aqueous phase was decanted by inverting the tube. To decrease the viscosity of the surfactant rich phase was dissolved in 300 μl of methanolic solution containing 0.1 M HNO₃. The resultant final solution was directly introduced in to the FAAS by conventional aspiration.

3.2. Determination of palladium in spiked and natural water samples

The extraction efficiency was studied using spiked water samples for the recovery of palladium. Doubly distilled water was spiked with known amounts of metal standards (5.0, 10.0 and 15.0 μg l⁻¹) and allowed to stand over night. The concentration of palladium in spiked water samples was determined.

The natural water samples filtered through a 0.45 μm pore size membrane filter to remove suspended particulate matter and then stored at 4 °C in the dark. To 10 ml of water sample 1.0 ml of solution containing 0.14% Triton X-114, and 0.004 M

Table 2
Determination of palladium in some synthetic alloys and in Pd–charcoal[a]

Sample	Speciality	Found (%), Pd
Alloy 1: Pd 95.4%, Ru 4.6%	High resistance to oxidation and corrosion	93.9 ± 0.7
Alloy 2: Pd 73%, Ag 25%, Ni 2%	Improvement in hardness and in resistance to mechanical wear	73.1 ± 0.2
Alloy 3: Pd 55%, Au 45%	Jewellery alloy	59.5 ± 0.8
Alloy 4: Pd 33%, Au 9%, Co 23%, Ni 35%	Low melting dental alloy	34.9 ± 0.7
Pd charcoal: Pd 11%, C 89%	Hydrogenation and dehydrogenation	9.9 ± 0.5

[a] Average of five determinations.

(NTACA) in ethanol and 3 ml of phosphate buffer were added. After phase separation 300 ml of a methanol solution containing 0.1 M HNO$_3$ was added to the surfactant rich phase. The final solution was determined by described in the above said general procedure.

3.3. Determination of palladium in synthetic alloys

Palladium in determined in certain synthetic mixtures corresponding to its alloys and in activated charcoal by using this method. The values are determined in good agreement with certified values as shown in Table 2.

4. Result and discussion

4.1. Pyrolysis and atomization temperature curves

Pyrolysis temperature and atomization temperature was investigated in the range of 300–1200 and 1700–2700 °C, respectively. When the pyrolysis temperature was close to 700 °C, the maximum relative integrated absorbance was achieved. When the temperature was further increased, the relative integrated absorbance decreases, increasing the atomization temperature to 2200 °C, the absorbance reached to the maximum. So, the pyrolysis temperature of 700 °C (Fig. 1) and atomization temperature of 2200 °C (Fig. 2) were selected for the further studies.

4.2. Effect of pH

pH is an important analytical parameter because, it shows the significant affects on the metal–ligand complex formation with sufficient hydrophobicity, which, able to extract into the small volume of surfactant-rich phase that results desired preconcentration of metal ions by cloud point extraction prior to FAAS. The effect of pH on the extraction efficiency by cloud point extraction was studied by adding 15 mg of each of the elements individually in to 250 ml sample solution in the pH range of 2.0–8.0 and the results shows that the maximum extraction efficiency was obtained at pH 6.0 ± 0.2, therefore, 6.0 ± 0.2 was
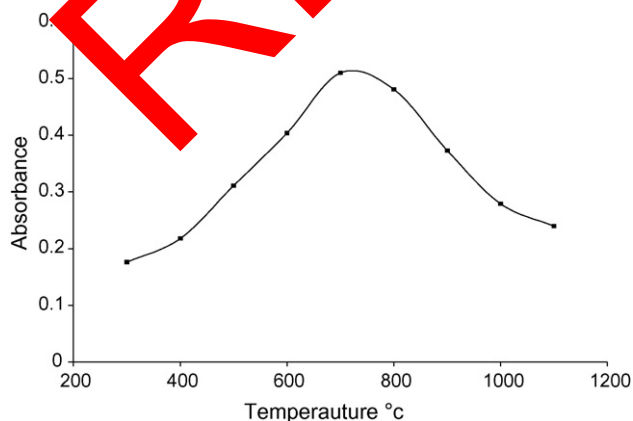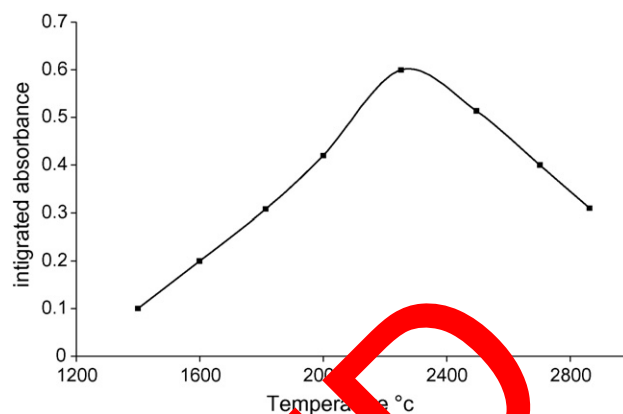

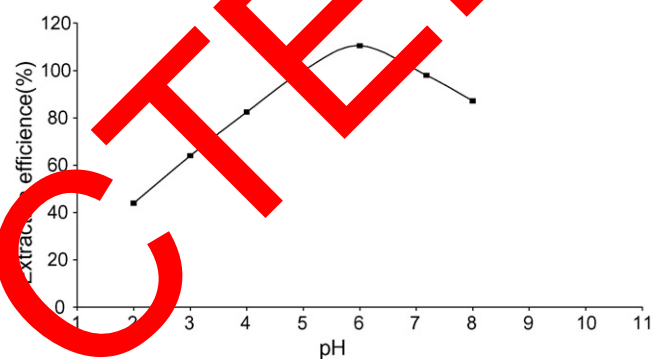Fig. 2. Atomization curve for the cloud point extraction of palladium.

Fig. 3. Effect of pH on the cloud point extraction for the determination of palladium.

selected for further investigation and the results were shown in Fig. 3.

4.3. Effect of 4-(2-naphthalenyl)thiozol-2yl azo chromotropic acid (NTACA) concentration

The effect of chelating reagent 4-(2-naphthalenyl)thiozol-2yl azo chromotropic acid (NTACA) concentration was studies by taking the range between 0.001 to 0.009 M and the results have shown in Fig. 4. At this initial point of the plateau it will be considered that the complete extraction was attained due to consumption of the reagent caused by its reactivity with other metal

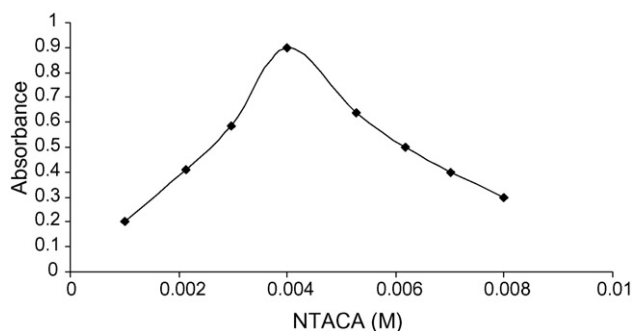Fig. 1. Pyrolysis curve for the cloud point extraction of palladium.

Fig. 4. Effect of NTACA concentration on cloud point extraction for the determination of palladium.
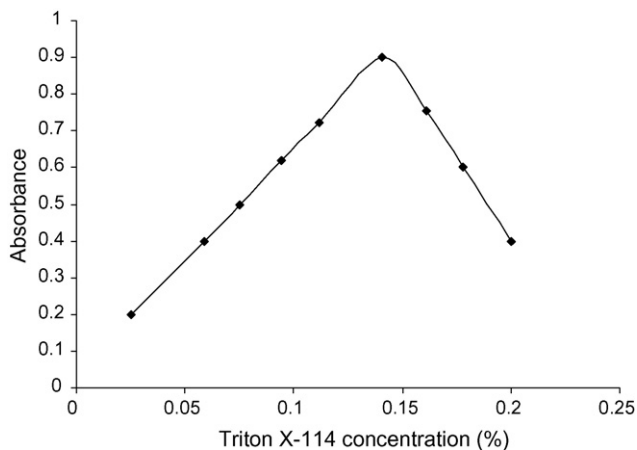
Fig. 5. Effect of Triton X-114 concentration on cloud point extraction for the determination of palladium.

ions which is required the addition of an excess of this chelating reagent. Therefore, 0.004 M of 4-(2-naphthalenyl)thiozol-2yl azo chromotropic acid (NTACA) solution was chosen further studies.

4.4. Effect of Triton X-114 concentration

Triton X-114 was chosen for the formation of the surfactant rich phase due to its low cloud point temperature (23–25 °C) and high density of the surfactant rich phase, which provide extraction efficiency in phase separation by centrifugation. The effect of Triton X-114 concentration was studied in the range of 0.04–0.20% (w/v). The extraction efficiency of analyte increased as the concentration of Triton X-114 increased from 0.04 to 0.20% (w/v) and it will remained constant between 0.12 and 0.14% (w/v). Therefore, 0.14% (w/v) of Triton X-114 was elected for the further studies and results were shown in Fig. 5.

4.5. Effect of equilibration temperature and incubation time

Incubation time and equilibration temperature about cloud point thoroughly investigated under optimized conditions with in the range of 30–60 °C and 10–15 min respectively. The maximum quantitative extraction was obtained at the temperature of 40 °C and equilibration time of 10 min. The effect of centrifugation time also increasing the extraction efficiency with in the range of 5–30 min. Ten minutes was selected as centrifugation time for quantitative extraction for entire procedure.

4.6. Effect of viscosity on analytical signal

The surfactant rich phase obtain after cloud point extraction is rather viscous, methanol contain 0.1 M nitric acid was added to the surfactant rich phase after separation of phase in order to facilitate its introduction into the nebuliser of the spectrometer an optimum volume of 300 μl methanolic solution of 0.1 M HNO_3 was added to the remaining micellar phase which shows the maximum analytical signal. The signal enhancement in the presence of organic solvents has been widely applied to increase

Table 3
Effect of foreign ions on the preconcentration and determination of palladium using cloud point extraction with NTACA

Ions	Concentration (mg l^{-1})
Mg^{2+}, K^+, Ni^{2+}, Cr^{2+}, Co^{2+}, Mn^{2+}, Br^-, HCO_3^-, F^-, SO_4^{3-}	4300
Zn^{2+}, I^-, Cd^{2+}, SCN^-, EDTA	3700
Ba^{2+a}, Pb^{2+a}	1000
Cu^{2+a}, Al^{3+a}, Fe^{3+a}, Fe^{2+a}	750
Ca^{2+a}	320
Sn^{2+}	140
	103
Pt^{4+}	12
Rh^{2+}	11

[a] As a masking agent (0.06 M EDTA)

the sensitivity during the analysis of a variety of metallic ions [39]. If the volume of methanol is lower than 300 μl then the signal is decreases due to the greater viscosity where as the added volume of methanol is higher than 300 μl it shows decrease in the signal. Hence, the 300 μl of methanol was chosen for further studies (Table 3).

4.7. Calibration precision and detection limits

The calibration graph was obtained by preconcentration of 250 ml sample in the presence of 0.14% Triton X-114 under the optimum instrumental condition. Table 4 shows the calibration parameters, the standard deviations obtained for 10 samples subjected to the complete procedure and the detection limit. The preconcentration factor was calculated as the ratio of the analyte after preconcentration to that prior to preconcentration which gives the same absorbance peak area (50-fold), for palladium 250 ml of sample volume. The precision of the method was established by repeated assays (n = 10) using 10 μg ml^{-1} solutions of analyte ions. The limit of detection was sufficiently low as compared that obtained by FAAS with out preconcentration limits around 0.067 ng ml^{-1}.

4.8. Effect of foreign ions

In view of the high selectivity and sensitivity provided by flame atomic absorption spectrometry, the only interfer-

Table 4
Analytical characteristics of present method

Preconcentration factor[a]	70
Correlation co-efficient (r)	0.9989
Regression equation, C (μg l^{-1})	Y = 15.07 × 10^{-3} + 0.017
LOD (ng ml^{-1})	0.67
Linear range (μg l^{-1})[b]	0.15–1.73
S.D. (%)[c]	0.0195

[a] Ratio of the concentration of analyte without the application of CPE technique to that after the CPE, giving the same analytical response.
[b] n = 9.
[c] For surfactant concentration (0.14 %, w/v).

Table 5

Determination of palladium in natural water samples using cloud point extraction

Samples	Palladium found[a] ($\mu g\,ml^{-1}$)	
	Present method	Spectrophotometric method [38]
Tap water-I[b] (*t*- and *f*-test)	0.060 ± 0.01 (−0.52 and 0.83)	0.048 ± 0.20
Tap water-II[b] (*t*- and *f*-test)	0.042 ± 0.01 (−2.92 and 0.96)	0.035 ± 0.01
River water-I[c] (*t*- and *f*-test)	0.32 ± 0.03 (2.37 and 0.67)	0.27 ± 0.04
River water-II[c] (*t*- and *f*-test)	0.25 ± 0.04 (2.51 and 0.77)	0.20 ± 0.03

[a] Mean ± S.D. (*n* = 10).
[b] Collected from Tirupati area, India.
[c] Collected from Swarnamukhi river, Srikalahasti, India.

Table 6

Recovery of palladium from spiked water samples using CPE technique

Element	Proposed method (concentration added)						Reported method [3?] (concentration added)					
	$5.0\,\mu g\,l^{-1}$		$10.0\,\mu g\,l^{-1}$		$15.0\,\mu g\,l^{-1}$		$5.0\,\mu g\,l^{-1}$		$10.0\,\mu g\,l^{-1}$		$15.0\,\mu g\,l^{-1}$	
	Found	Recovery (%)[a]	Found	Recovery (%)[a]	Found	Recovery (%)[a]	Found	Recovery (%)[a]	Found	Recovery (%)[a]	Found	Recovery (%)[a]
Palladium	4.85	97.00 ± 0.28	9.89	98.9 ± 0.34	14.85	99.00 ± 0.42	4.7?	95.0? ± 0.23	9.72	97.20 ± 0.37	14.65	97.60 ± 0.50
t- and *f*-test		8.83 and 0.66		−1.87 and 0.86		−8.24 and 0.69						

[a] Mean ± S.D. (*n* = 6).

Table 7

Comparison of the present method with reported methods for the preconcentration and CPE of palladium

Reagent	Surfactant	Technique	Detection limit	Reference
1-(2-Thiazolylazo)-2-naphthol	TritonX-114	FAAS	$0.24\,ng\,ml^{-1}$	[40]
Ammonium pyrroline dithiocarbamate	TritonX-114	GFAAS	$0.1–2.0\,\mu g\,ml^{-1}$	[41]
1-(2-Pyridylazo)-2-naphthol	TritonX-114	FAAS	$0.38\,ng\,ml^{-1}$	[42]
2-(5-Bromo-2-pyridylazo-5(diethylamino)-phenol)	TritonX-114	GFAAS	$0.08\,\mu g\,ml^{-1}$	[43]
8-Hydroxyquinoline	TritonX-114	GFAAS	$0.012\,ng\,ml^{-1}$	[44]
1-Nitroso-2-naphthol	PONPE 7.5	FAAS	$1.22\,\mu g\,ml^{-1}$	[45]
N-Benzoyl-*N*-phenyl hydroxylamine	TritonX-114	FAAS	$2.08\,ng\,ml^{-1}$	[46]
1-Phenyl-3-methyl-4-benzoyl-5-pyrazolone	TritonX-100	FAAS	$0.64\,ng\,ml^{-1}$	[47]
4-(2-Naphthalenyl)thiozol-2yl azo chromotropic acid	TritonX-114	FAAS	$0.067\,ng\,ml^{-1}$	Present work

ence studied were those related to the preconcentration step. The influence of foreign ions on the determination of palladium was studied an error of ±2% in absorbance reading was considered tolerance. Sample solution containing palladium (50 $\mu g\,l^{-1}$) and other ions were prepared and the developed procedure was applied. The tolerance limits of various foreign ion are given in Table 5 and prove that the recoveries of analyte ions in almost quantitative in the presence of interfering cations.

4.9. Application of present method and statistical comparison with reported method

The data obtained from proposed method for the preconcentration and cloud point extraction applied for spiked and natural water samples were represented in Tables 5 and 6. The results obtained from natural water samples was compared with the spectrophotometric method in terms of Student's '*t*'-test and variance ratio of '*f*'-test suggest that percentage recovery of palladium from water samples ranges from 96.7 to 99.4% which is more reliable and sensitive than the reported method. Present

method was compared with the reported methods in the literature in terms of detection limits and instruments employed for the analysis of metal ions in various environmental samples. It is evident from the data in Table 7 that the proposed method is rapid, more sensitive and selective.

5. Conclusion

The cloud point extractions offers a simple rapid sensitive inexpensive, non-polluting and environmentally begin methodology which is alternative to other separation/preconcentration technique in various water samples. This method has added advantages over reported method (Table 7):

(i) The synthesis of metal chelating agent at ordinary laboratory was simple and more economical.
(ii) The synthesis of organic reagent is distancing in terms of sensitivity, selectivity to wards metal ions.
(iii) The risk of contamination is quite low.
(iv) Foreign ion does not interfere in proposed method, which is making the method selective.

(v) The proposed CPE method gives very low LOD, good SD's and solvent free extraction of the elements from its initial matrix.

(vi) The proposed method is successfully applied for the determination of palladium in water samples.

(vii) Triton X-114 was chosen for the formation of the surfactant rich phase due to its excellent physico-chemical characteristics.

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