

## Determination of Palladium in Water Samples Using Cloud Point Extraction Coupled with Laser Thermal Lens Spectrometry

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**ABSTRACT.** A preconcentration procedure for determination of palladium by laser thermal lens spectrometry (TLS) is proposed. It is based on cloud point extraction of palladium(II) ions as 2-(3,5-dichloro-2-pyridylazo)-5-dimethylaminoaniline (3,5-diCl-PADMA) complexes using octylphenoxypolyethoxyethanol (Triton X-114) as surfactant. The effects of various experimental conditions such as pH, concentration of ligand and surfactant, equilibration temperature and time on cloud point extraction were studied. Under the optimized conditions, the calibration graph was linear in the range of 0.15–6 ng mL<sup>-1</sup>, and the detection limit was 0.04 ng mL<sup>-1</sup> with an enrichment factor of 22. The sensitivity was enhanced by 846 times when compared with the conventional spectrophotometric method. The recovery of palladium was in the range of 96.6%–104.0%. The proposed method was applied to the determination of palladium in water samples.

**Key words:** Cloud point extraction, Palladium, Triton X-114, 2-(3,5-Dichloro-2-pyridylazo)-5-dimethylaminoaniline, Laser thermal lens spectrometry

### 1. INTRODUCTION

Palladium, as a precious metal, plays a very important role in modern industry due to its attractive physical and chemical properties, such as excellent corrosion resistance, stable thermoelectricity and high catalytic activity. It has been widely used in various ways as a micro-contact in electronics, as an alloy in the production of dental and medicinal devices, and as a catalyst in hydrogenation, dehydrogenation and organic synthesis. In last few decades, palladium has also been used as a component in the three-way catalysts in automotive catalytic converters. It is reported currently that more than 50% of the world's production of palladium are being consumed in production of auto-catalysts each year since palladium was introduced to catalytic converters.<sup>1</sup> Due to the extended use of palladium in catalytic converters in motor vehicles, the emission of this metal into the environment has increased considerably.<sup>2</sup> Under appropriate conditions, such as pH and redox potential, it is assumed that palladium undergoes methylation reactions in the aquatic environment and could be concentrated along the food chain, resulting in ecological and human health risks.<sup>3,4</sup> Consequently, establishing simple, highly sensitive and selective method for the determination of trace amounts of palladium in water samples is of great importance. However, it is often not possible to make direct determinations of palladium by employing the known analytical tech-

niques due to its low or even extremely low concentration as well as matrix effects.<sup>1</sup> Pre-concentration and separation coupled with highly sensitive technique is one of the best ways to solve these problems. There are many approaches for preconcentration and separation, such as liquid-liquid extraction,<sup>5,6</sup> solid phase extraction,<sup>7–9</sup> ion exchange<sup>10,11</sup> and HPLC.<sup>12</sup>

Cloud point extraction (CPE) is a new type of environmental extraction technique with many advantages, such as low cost, safety, simplicity and a high concentration factor. Also, CPE does not use toxic organic solvent compared with the traditional liquid-liquid extraction method.<sup>13</sup> CPE is in agreement with the "green chemistry" principle,<sup>14</sup> and has been used for separation/preconcentration of trace metals after the formation of sparingly water-soluble complexes.<sup>15–19</sup>

Laser thermal lens spectrometry (TLS) is one of the photothermal analytical techniques developed in the late 1970s and early 1980s.<sup>20–23</sup> It is based on the measurement of changes in the refractive index of medium upon the absorption of laser radiation, proportional to the concentration of the absorbent. This method allows for the measurement of absorbances as small as 10<sup>-8</sup>–10<sup>-6</sup> or for the determination of analytes at concentrations as low as 10<sup>-11</sup>–10<sup>-9</sup> mol L<sup>-1</sup>.<sup>23,24</sup> TLS is well known for its high sensitivity.

Therefore, the combination of CPE, as a highly efficient separation and preconcentration approach, with TLS, as a highly sensitive detection technique, shows much prom-

ise for trace analysis, especially with extremely low concentration and complex matrices. However, there are few data on the combination of CPE with TLS so far.<sup>25–27</sup> In this paper, a new method for the determination of trace amounts of palladium in water samples using CPE coupled with TLS has been developed. In the developed method, 2-(3,5-dichloro-2-pyridylazo)-5-dimethylaminoaniline (3,5-diCl-PADMA) was adopted as the chelating reagent for it was found to be a good chromogenic reagent for the determination of palladium<sup>28</sup> and the maximum absorption wavelength of its palladium complex (623 nm) is well matched with the wavelength of the He-Ne laser (632.8 nm), and octylphenoxypolyethoxyethanol (Triton X-114) as the extractant for it has a very convenient cloud point (in the range of 23–25 °C). Potential factors affecting the CPE separation and preconcentration palladium (II) and the method sensitivity were investigated in detail. The proposed method was applied to the determination of trace amounts of palladium in water samples.

## EXPERIMENTAL

### Instrumentation

Thermal lens measurements were performed on a laboratory-made single laser thermal lens spectrometer described in detail previously.<sup>29</sup> A PS-THN-1200 He-Ne laser (Shanling Laser and Electronic Appliance Co. Ltd. China) with  $\lambda=632.8$  nm (TEM00 mode, 25 mW) was exploited as both excitation and probe beam. A model 197 chopper (Ametek Advanced Measurement Technology Company, USA) was used to modulate the laser beam at 10 Hz. After being focused by a 150 mm focal length lens, the laser beam passed through a 5 mm optical path length quartz cell located at the confocal distance. The signal was measured as the beam center intensity as a function of time change using a photoelectric device located at 2.4 m distance from the sample cell and behind a 0.5 mm pinhole. A DS5102M digital storage oscilloscope (Benjing Rigol Electronic Co. Ltd., China) connected to a personal computer was used to digitize and process the output signal from the photoelectric device.

A TU-1810 spectrophotometer (Beijing Puxi Genaral Co. Ltd. China) equipped with a 1 cm quartz cell was used for absorption Spectra measurements. pH values were determined with a PHS-2C digital pH meter supplied with a combined glass electrode (Shanghai Leici Instruments Factory, China). A HH-2 thermostatic bath (Beijing Kewei Yongxing Instrument Co. LTD., China), maintained at the desired temperature, was used to for cloud point preconcentration experiments. Phase separation process was accelerated by

a model 800 centrifuge (Shanghai Pudong Physical Instruments Factory, China).

### Reagents

A standard stock solution of palladium (1000  $\mu\text{g/mL}$ ) was prepared by dissolving 0.1000 g of spectrographically pure palladium in 50 mL of aqua regia, adding 1 mL 20% NaCl, heating almost to dryness, then adding 2 mL concentrated HCl, evaporated to nearly dryness, dissolving the residue in 6 mol L<sup>-1</sup> HCl, and diluting to 100 mL with 6 mol L<sup>-1</sup> HCl. The working solutions were obtained by stepwise dilution of this solution with water.

A  $5 \times 10^{-4}$  mol L<sup>-1</sup> 3,5-diCl-PADMA (laboratory-synthesized [30]) ethanol solution was prepared by dissolving appropriate amounts of this reagent in absolute ethanol. A 1% (weight/volume, w/v) Triton X-114 (Sigma-Aldrich, Milwaukee, USA) water solution was prepared. Buffer solution of pH 4.5 was prepared by mixing appropriate ratios of a 0.2 mol L<sup>-1</sup> HAc and 0.2 mol L<sup>-1</sup> NaAc. A 2 mol L<sup>-1</sup> HClO<sub>4</sub>-alcohol solution was prepared by mixing 6 mol L<sup>-1</sup> HClO<sub>4</sub> solution and ethanol with a volume proportion of 1:2. Doubly distilled water was used for all preparations of the standard and sample solutions. All the chemicals used were of analytical reagent grade unless otherwise stated.

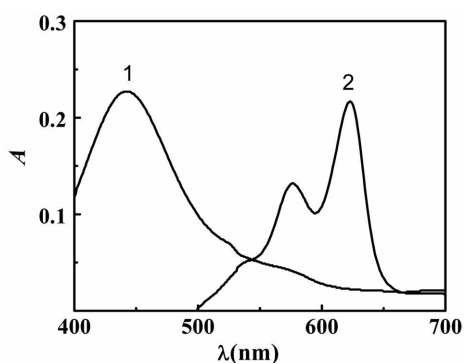
### General Procedure

An aliquot of a solution containing appropriate amounts of palladium, 2 mL pH 4.5 HAc-NaAc buffer solution, 80  $\mu\text{L}$  of  $5.0 \times 10^{-4}$  mol L<sup>-1</sup> 3,5-diCl-PADMA solution and 0.6 mL of 1% (w/v) Triton X-114 solution were transferred into a 10-mL graduated conical centrifuge tube. The mixture was diluted to 10 mL with water. The resultant solution was shaken and kept in a thermostatic water bath maintained at 60 °C for 15 min. Then, the turbid solution was centrifuged for 5 min at 3500 rpm for phase separation. After cooling in an ice-bath for 10 min, the surfactant-rich phase retained at the bottom of the tube became viscous and the bulk aqueous phase was easily decanted simply by inverting the tube. The surfactant phase in the tube was dissolved with 0.45 mL 2 mol L<sup>-1</sup> HClO<sub>4</sub>-alcohol solution. The final solution was transferred into a 5 mm optical path length quartz cell to measure the thermal lens signal ( $S_c$ ) at wavelength of 632.8 nm and the chopper frequency of 10 Hz by the thermal lens spectrometer.

## RESULTS AND DISCUSSION

### Absorption Spectra and the Selection of Wavelength

The absorption spectra of 3,5-diCl-PADMA and Pd(II)-

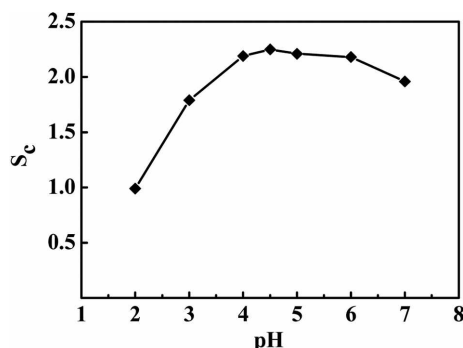


**Figure 1.** Absorption spectra. 1. 3,5-diCl-PADMA vs water; 2. Pd(II)-3,5-diCl-PADMA vs reagent blank. Conditions:  $1.0 \times 10^{-5}$  mol L $^{-1}$  3,5-diCl-PADMA;  $100$  ng mL $^{-1}$  Pd $^{2+}$ .

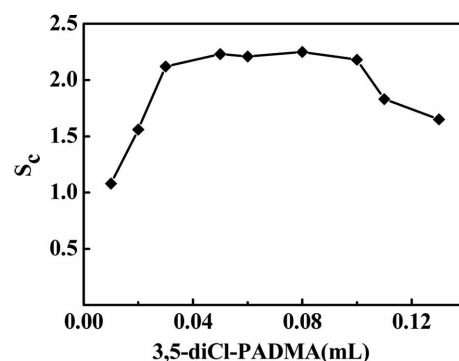
3,5-diCl-PADMA complex in the surfactant phases after dissolving with HClO $_4$ -ethanol solution were recorded (Fig. 1). 3,5-diCl-PADMA itself shows a maximum absorption at 443 nm. Pd(II)-3,5-diCl-PADMA complex shows a maximum absorption at 623 nm which is well matched to the wavelength of the He-Ne laser (632.8 nm).

### Effect of pH

The chelating agent 3,5-diCl-PADMA exists in four species H $_3$ R $^+$ , H $_2$ R $^{2+}$ , HR $^+$ , and R in the solution, with protonation of the ring nitrogen and the two amino group nitrogen atoms. The concentration distribution of the four species in solution is determined by the acidity. Therefore, the pH of the solution affected not only the formation, but also the hydrophobicity of the chelate. The effect of pH upon the preconcentration of Pd was tested in the pH range of range 2.0–7.0 buffer solution and the results are shown in Fig. 2. It can be seen that a plateau thermal lens signal was obtained in the pH range of 4.0–6.0. Hence, a pH of 4.5 was chosen for subsequent investigation.



**Figure 2.** Effect of pH on the thermal lens signal. Conditions:  $80$   $\mu$ L  $5 \times 10^{-4}$  mol L $^{-1}$  3,5-diCl-PADMA;  $0.6$  mL  $1.0\%$  (w/v) Triton X-114; temperature:  $60$   $^{\circ}$ C; heating time:  $15$  min;  $3.5$  ng mL $^{-1}$  Pd $^{2+}$ .



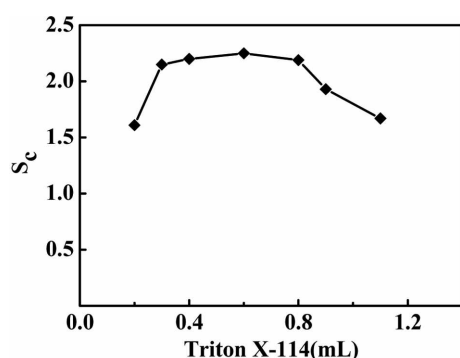
**Figure 3.** Effect of the amount of 3,5-diCl-PADMA on the thermal lens signal. Conditions:  $5.0 \times 10^{-4}$  mol L $^{-1}$  3,5-diCl-PADMA;  $0.6$  mL  $1.0\%$  (w/v) Triton X-114; temperature:  $60$   $^{\circ}$ C; heating time:  $15$  min;  $3.5$  ng mL $^{-1}$  Pd $^{2+}$ ; pH 4.5.

### Influence of Chelating Agent

It was found that 3,5-diCl-PADMA concentration used in the experiment affected the extraction of Pd because 3,5-diCl-PADMA was prepared by the solvent absolute ethanol. The lower the concentration of 3,5-diCl-PADMA solution, the larger volume of its solution will be used. This means that more absolute ethanol will enter the CPE system, which will prevent the micelle formation and reduce the extraction efficiency. In order to reduce the volume added, relatively higher concentration of 3,5-diCl-PADMA solution  $5.0 \times 10^{-4}$  mol L $^{-1}$  was chosen. Then, the effect of the amount of 3,5-diCl-PADMA on the analytical performance was investigated in the range of  $10$ – $140$   $\mu$ L. As shown in Fig. 3, the thermal lens signal firstly increased as the volume of 3,5-diCl-PADMA increased and then keeps almost stable in the range of  $30$ – $100$   $\mu$ L 3,5-diCl-PADMA. But the signal began to decrease when the volume of 3,5-diCl-PADMA is over  $100$   $\mu$ L. This is because 3,5-diCl-PADMA also has strong hydrophobicity, there was more 3,5-diCl-PADMA and less Pd(II)-3,5-diCl-PADMA complex in the surfactant-rich phase with the further increasing of amounts of 3,5-diCl-PADMA. Hence,  $80$   $\mu$ L of  $5.0 \times 10^{-4}$  mol L $^{-1}$  3,5-diCl-PADMA was chosen for subsequent experiments.

### Effect of the Amount of Triton X-114

Triton X-114 was chosen as the extractant due to its commercial availability in a highly purified homogeneous form, convenient cloud point temperature ( $23$ – $25$   $^{\circ}$ C), low toxicity and cost, and high density of the surfactant-rich phase which facilitates phase separation by centrifugation. The amount of Triton X-114 not only affected the extraction efficiency, but also the volume of surfactant-rich phase. The effect of the amount of Triton X-114 on the thermal lens signal of the system was investigated. The results are



**Figure 4.** Effect of the amount of Triton X-114 on the thermal lens signal. Conditions: 0.08 mL  $5 \times 10^{-4}$  mol L $^{-1}$  3,5-diCl-PADMA; temperature: 60 °C; heating time: 15 min; 3.5 ng mL $^{-1}$  Pd $^{2+}$ ; pH 4.5.

shown in Fig. 4. As can be seen, the thermal lens signal increased initially with the amount of 1.0% (w/v) Triton X-114 and then remained nearly constant in the volume range of 0.3–0.8 mL Triton X-114. But when the amount of Triton X-100 was above 0.8 mL, the signal decreased because of the increment in the volume of the surfactant phase. Therefore, 0.6 mL of 1% (w/v) Triton X-114 used in subsequent experiments.

#### Effect of Equilibration Temperature and Time

The cloud point temperature of Triton X-114 is between 23 and 25 °C in the concentration range 0.1–5% (w/v), but overheating by at least more than 15–20 °C is essential for extraction and efficient separation of the phases. The influence of equilibration temperature on thermal lens signal was studied by varying the temperature in the range of 40–80 °C. The results showed that when the temperature is higher than 50 °C, good phase separation could be obtained and the thermal lens signal showed no obvious change. Therefore, 60 °C was selected for all experiments. The dependence of thermal lens signal upon equilibration time was also investigated for a time interval of 5–30 min. It was found that when the equilibrium temperature was fixed at 60 °C, the thermal lens signal was essentially constant after 15 min. Hence, 15 min of equilibration time was finally selected.

#### Effect of Perchloric Acid and Organic Solvent

The synthesis of the chelating agent 3,5-diCl-PADMA and its color reaction with Pd(II) have been reported in previous works.<sup>28,30</sup> It was showed that Pd(II) could react with 3,5-diCl-PADMA either in strong acidic media (0.5–4.8 mol L $^{-1}$  HClO $_4$ ) to directly form a blue diproton complex (PdRH $_2^{2+}$ ,  $\lambda_{\text{max}}$  616 nm) possessing higher absorption characteristic, or in weak acidic media to form a red complex (PdR) which, when formed, could be changed into the species

PdRH $_2^{2+}$  after acidification with HClO $_4$ . Although the reaction taking place directly in strong acidic media has higher selectivity, the species PdRH $_2^{2+}$  formed has strong hydrophilicity and is not easily extracted into the surfactant-rich phase. For this reason, in this study, we choose to let the reaction of Pd(II) with 3,5-diCl-PADMA and the cloud point extraction perform in weak acidic media (pH 4.5), then acidified the remaining phase by HClO $_4$  after phase separation to change the species PdR into the species PdRH $_2^{2+}$ .

In addition, the thermal lens signal is very sensitive to the thermo-optical properties of the medium, including temperature dependent refractive index ( $dn/dT$ ) and thermal conductivity ( $k$ ).<sup>31,32</sup> Owing to its low  $dn/dT$  and  $k$  value, water is a poor solvent for TLS. On the contrary, organic solvents have much better thermo-optical properties than water due to higher  $dn/dT$  and  $k$  values. In order to enhance the thermal lens signal as well as match the wavelength of the laser beam used (632.8 nm), the surfactant-rich phase after CPE should be dissolved with HClO $_4$  as well as organic solvent. The organic solvent chosen should have high signal enhancement factor and be environmental friendly, and be readily soluble with HClO $_4$ . In addition, the maximum absorption wavelength of the complex PdRH $_2^{2+}$  in the selected solvent should be as close as possible to the wavelength of the laser beam used. In the common used solvent, ethanol can be met all the requirements mentioned above. Therefore, HClO $_4$ -ethanol solution was selected as solvent medium for dissolving the remaining phase as well as for TLS measurement. In the selected medium, the palladium complex PdRH $_2^{2+}$  exhibits a maximum absorption peak at 623 nm which is well matched to the wavelength of the He-Ne laser (632.8 nm).

#### Analytical Performance of the Method

Under the optimal experimental conditions, the calibration curve obtained by the proposed method was linear in the range of 0.15–6.0 ng mL $^{-1}$ . The linear equation was  $S_L = 0.6662c - 0.0755$ , with a correlation coefficient  $r = 0.9971$ , where  $c$  is the concentration of Pd in ng mL $^{-1}$ . The detection limit, calculated as three times the standard deviation of the blank solution ( $3\sigma$ ), was 0.04 ng mL $^{-1}$ . Compared with the general spectrophotometric method,<sup>28</sup> the sensitivity of this method was increased by 846 times calculated as the ratio of the slopes of the calibration graphs. The enrichment factor, defined as the ratio of the volumes before and after CPE, was 22.

A comparison of the present method with other reported cloud point extraction methods is given in Table 1. Further improvement of the detection limit is also feasible, either

**Table 1.** Comparison of the present method with reported methods for CPE of palladium

Reagent	Detection system	Surfactant	DL (ng·mL <sup>-1</sup> )	Ref.
4,4'-Bis(dimethylamino) thiobenzophenone (Thio-Michler's Ketone, TMK)	SP	Triton X-114	0.47	33
1-(2-Pyrisylazo)-2-naphthol (PAN)	FAAS	Triton X-100	0.3	34
Bis((1 <i>H</i> -benzo [d] imidazol-2-yl)ethyl) sulfane (BIES)	FAAS	Triton X-114	1.6	35
2-((2-((1 <i>H</i> -benzo[d]imidazole-2-yl)methoxy)phenoxy)methyl)-1 <i>H</i> -benzo[d]imidazol (BIMPI)	FAAS	Triton X-114	25	36
1-(2-Pyrisylazo)-2-naphthol (PAN)	FAAS	Triton X-114	3.4	37
Dimethylglyoxime	FJ-FAAS	Triton X-114	1.0	38
Ammonium pyrrolisidine dithiocarbamate (APDC)	FAAS	Tergitol TMN-6	1.4	39
1-Phenyl-3-methyl-4-benzoyl-5-pyrazolone (PMBP)	FAAS	PONPE 7.5	1.8	16
2-(5-Bromo-2-pyridylazo)-5-diethylaminophenol(5-Br-PADAP)	CZE-DAD	PONPE 7.5	0.08	40
<i>O,O</i> -diethyldithiophosphate (DDTP)	ETAAS	Triton X-114	0.014	41
Benzil mono-(2-pyridyl) hydrazone	GFAAS	Triton X-114	0.12	42
2-Mercaptobenzothiazole (2-MBT)	ICP-MS	Triton X-100	5	43
2-(3,5-Dichloro-2-pyridylazo)-5-dimethylaminoaniline (3,5-diCl-PADMA)	TLS	Triton X-114	0.04	This work

**Table 2.** Effect of foreign ions on determination of Pd by CPE

Ions	Mass ratio of foreign ion to Pd	Ions	Mass ratio of foreign ion to Pd
Ca <sup>2+</sup>	4000	Mo (VI)	300
K <sup>+</sup>	2000	Br <sup>-</sup>	300
Sr <sup>2+</sup>	1500	NaF	300
F <sup>-</sup>	1500	Al <sup>3+</sup>	100
SO <sub>4</sub> <sup>2-</sup>	1500	Cr <sup>3+</sup>	100
Ba <sup>2+</sup>	1000	Ir (IV)	100
Cd <sup>2+</sup>	1000	Fe <sup>3+</sup>	100
NO <sub>3</sub> <sup>-</sup>	1000	Na <sub>4</sub> P <sub>2</sub> O <sub>7</sub>	100
As (V)	600	Thiourea	100
Mg <sup>2+</sup>	500	Cu <sup>2+</sup>	50
Zn <sup>2+</sup>	500	W (VI)	50
La <sup>3+</sup>	500	Hg <sup>2+</sup>	10
Mn <sup>2+</sup>	300	Os (VI)	10
Sn (IV)	300		

\*Masked with 0.1 mL 30 µg/mL Na<sub>4</sub>P<sub>2</sub>O<sub>7</sub> solution.

by preconcentration of larger amounts of the sample solution or diluting the surfactant rich phase to a smaller volume.

### Interferences

The effects of foreign species on the determination of 3.5 ng/mL palladium ions by the proposed method were tested. A foreign species was considered to be interfering when it caused a variation greater than  $\pm 5\%$  in the thermal lens signal of the sample. The tolerance limits of various foreign species were shown in Table 2.

### Determination of Pd in Real Water Samples

The proposed method was applied to the determination of palladium in tap, river and well water samples. For each water sample, 5 mL of water sample was taken in a 10 mL graduated conical centrifuge tube, and 0.1 mL 30 µg/mL Na<sub>4</sub>P<sub>2</sub>O<sub>7</sub> solution was added. Then the determination was continued according to the procedure. Addition/recovery

**Table 3.** Determination results of palladium in water samples

Sample Number	Sample	Added (ng mL <sup>-1</sup> )	Found (ng mL <sup>-1</sup> )	RSD (%) ( <i>n</i> =6)	Recovery (%)
W100301	Tape water	2.0	1.94	4.2	97.0
		4.0	3.97	2.1	99.2
W100303	Well water	1.5	1.56	1.8	104.0
		3.5	3.44	3.8	98.3
W100304	River water	3.0	3.10	4.5	103.3
		5.0	4.83	3.6	96.6

W100301: The concentration of Fe<sup>3+</sup> and Mn<sup>2+</sup> was 30 and 10 ng mL<sup>-1</sup> respectively, and Pb<sup>2+</sup>, Cu<sup>2+</sup>, Zn<sup>2+</sup> and Cd<sup>2+</sup> were lower than 200, 50, 50 and 50 ng mL<sup>-1</sup> in the water sample, respectively; W100303: The concentration of Mn<sup>2+</sup> was 10 ng mL<sup>-1</sup>, and Fe<sup>3+</sup>, Pb<sup>2+</sup>, Cu<sup>2+</sup>, Zn<sup>2+</sup> and Cd<sup>2+</sup> were lower than 30, 200, 50, 50 and 50 ng mL<sup>-1</sup> in the water sample, respectively; W100304: The concentration of Fe<sup>3+</sup>, Cu<sup>2+</sup>, Mn<sup>2+</sup> was 30, 50 and 230 ng mL<sup>-1</sup>, and Pb<sup>2+</sup>, Zn<sup>2+</sup> and Cd<sup>2+</sup> were lower than 50 ng mL<sup>-1</sup>. All the water samples and their analytical results were provided by Xi'an Hydrographic Bureau, Xi'an, Shaanxi Province, China.

tests were also performed, and the analytical results and the recovery are shown in Table 3. The recoveries are between 96.6% and 104.0%, indicating the accuracy and applicability of the proposed method for the determination of palladium in the in the real water samples.

## CONCLUSION

In this work, we proposed a new method for the determination of palladium by CPE combined with TLS using 3,5-diCl- PADMA as chelating reagent and the nonionic surfactant of Triton X-114 as extractant. The combination is favorable because CPE is an easy, safe, rapid, economical and eco-friendly methodology for preconcentration and separation of trace metals in aqueous solutions, and TLS is a highly sensitive detection technique. Triton X-114 was selected for the formation of the surfactant-rich phase due to its excellent physicochemical characteristics: convenient cloud point temperature, high density of the surfactant-rich phase which facilitates phase separation by centrifugation. 3,5-diCl-PADMA was chosen as the chelating reagent because it is a good chromogenic reagent for palladium, and the maximum absorption wavelength (623 nm) of its palladium complex is well match with the output wavelength (632.8 nm) of the He-Ne laser.

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