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ISSN: 0973-4945; CODEN ECJHAO
E-Journal of Chemistry
2009, **6(4),** 1077-1084

Homogeneous Liquid-Liquid Extraction Method for Selective Separation and Preconcentration of Trace Amounts of Palladium

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Received 25 January 2009; Accepted 20 March 2009

Abstract: A simple and effective homogeneous liquid-liquid extraction method for selective separation, preconcentration and spectrophotometric determination of palladium(II) ion was developed by using a ternary component system (water / tetrabutylammonium ion (TBA^+) / chloroform). The phase separation phenomenon occurred by an ion–pair formation of TBA^+ and perchlorate ion. Thio-Michler's ketone (TMK), 4, 4′-bis (dimethylamino) thiobenzophenone, was used as a complexing agent. After optimization of complexation and extraction conditions ([TMK] = 5.0×10^{-5} mol L^{-1}, [TBA^+] = 2.0×10^{-2} mol L^{-1}, [$CHCl_3$] = 60.0 µL, [ClO_4^-] = 2.5×10^{-2} mol L^{-1} and pH= 3.0), a preconcentration factor 10 was obtained for 10 mL of sample. The analytical curve was linear in the range of 2-100 ng mL^{-1} and the limit of detection was 0.4 ng mL^{-1}. The relative standard deviation was 3.2% (n=10). Accuracy and application of the method was estimated by using test samples of natural and synthetic water spiked with different amounts of palladium(II) ion. The method is very simple and inexpensive.

Keywords: Liquid-liquid extraction, Palladium, Preconcentration, Thio-Michler's ketone (TMK).

Introduction

Palladium was used in different areas of science and technology, including coating agents, brazing alloys, petroleum, electrical industries and catalytic reactions[1,2]. Thus, due to its increasing

use on one hand, and the toxicity of Pd(II) compound to mammals, fish, and higher plants on the other hand[3], determination of palladium is of special interest in environmental analysis.

Because of low concentration of Pd in industrial (μg g^{-1} level) and environmental samples (ng g^{-1} level) and complexity of the matrix, elaboration and application of preconcentration / matrix separation procedures is necessary before detection of the analyte. For this purpose, systems based on liquid-liquid extraction[4-6] ion exchange[7-9], solid sorbent extraction[10-12], electrochemical deposition[13,14], precipitation and co-precipitation[15] and micellar system[16] have been used.

However, these methods are typically time-consuming and labor-intensive, have multi-step procedures prone to loss of analytes and need high volumes of samples. Therefore, simple, rapid and efficient techniques that can be preformed easily are required.

Homogeneous liquid-liquid extraction is an excellent method that extracts desired solute existing in the homogeneous solution into the water–immiscible phase by each kind of phase separation phenomenon. In homogeneous liquid-liquid extraction, the initial condition (before phase separation) is homogeneous solution; namely, there is no interface between the water phase and organic solvent phase. In other words, the surface area of the interface is infinitely large initially. Accordingly, no vigorous mechanical shaking is necessary. The procedure is simple, rapid and requires only the addition of the reagents[17].

The methods, which used the phase separation depends upon the temperature of the water–propylene carbonate system[18] or the salt effect in the water–acetonitrile system, *etc*., have already been reported[19].

Recently, homogeneous liquid-liquid extraction method using a ternary solvent system has been developed[17] and it was applied as a simple and high-powered preconcentration for the instrumental analysis[20-23]. In concretely, the methods based on the pH dependent phase separation, which used a water / acetic acid / chloroform ternary solvent system[20] and water / pyridine / ethyl chloroacetate system[24] were reported. However, in these methods, the widespread application for target analytes has been limited by the inconvenient pH condition in extraction.

Recently, a pH independent phase separation phenomenon using the ion-pair formation of tetrabutylammonium ion (TBA^+) and perchlorate (ClO_4^-) in homogeneous solution (water / TBA^+/ chloroform) has been reported. In this method, chloroform is solvated by TBA^+ and dissolves in water. When $NaClO_4$ is added to the homogeneous solution that consists of a water / TBA^+/ chloroform, the salvation effect of TBA^+ is excluded by ion-pair formation of TBA^+ and ClO_4^-. Therefore, the chloroform in homogeneous aqueous solution is postulated to form water-immiscible chloroform in aqueous solution by the phase separation[25,26].

In the present work, homogeneous liquid-liquid extraction, using Thio-Michler's ketone (TMK), 4,4′-bis(dimethylamino) thiobenzophenone, as a complexing agent and water / TBA^+/ chloroform ternary component system, was applied to the separation and preconcentration of trace amounts of Pd(II) in natural water samples and its spectrophotometric determination.

Experimental

Absorbance measurements were carried out with a Shimadzu UV-2550 double–beam spectrophotometer and a 1 mL quartz cell at 518 nm (λ_{max}). Phase separation was assisted using a centrifuge (centurion scientific Ltd model: 1020D). The pH of the solutions was controlled with Metrohm pH-meter model 713.

Reagents and solutions

All reagents used were of analytical grade. Stock solution of palladium (1000 mg L^{-1}) was prepared by dissolving appropriate amounts of metallic Pd in aqua regia. Working solutions were prepared from the stock solution by serial dilutions with doubly distilled water.

Other reagents used were tetrabutylammonium bromid (Merck), chelating agent TMK (Merck), nitric and hydrochloric acid (Merck), sodium hydroxide and sodium perchlorate (Merck). Chloroform and ethanol were of analytical - grade from Merck.

A stock standard buffer solution, 0.1 mol L^{-1} was prepared by dissolving appropriate amount of sodium acetate and hydrochloric acid. The pipettes and vessels used for trace analysis were kept in 10% nitric acid for at least 24 h and subsequently washed four times with deionized water before use.

Homogeneous liquid-liquid extraction and quantification of palladium(II)

10 mL homogeneous solution (water / TBA^+ / chloroform) containing analyte (2-100 ng mL^{-1}), chloroform (60.0 µL), TMK (5.0×10^{-5} mol L^{-1}), TBA^+ (2.0×10^{-2} mol L^{-1}) and 2.0×10^{-3} mol L^{-1} acetate buffer (pH = 3.0) were kept in a thermostated bath at 25 °C for 5 min. An aqueous solution of $NaClO_4$ (2.5×10^{-2} mol L^{-1}) was added and the mixture was gently shaken. The mixture was then centrifuged for 3 min at 4000 rpm.

The sediment phase (50 µL) was separated using a 100 µL micro-syringe, transferred into a spectrophotometer cell and diluted to 1 mL with ethanol. The palladium concentration was then determined at 518 nm against a reagent blank.

Results and Discussion

Effect of pH

The separation of metal ions by homogeneous liquid-liquid extraction involves prior formation of a complex with sufficient hydrophobicity to be extracted into the small volume of sediment phase; thus obtaining the desired preconcentration. pH plays an unique role on metal-chelate formation and subsequent extraction. The effect of pH on the extraction of palladium from water samples was studied in the pH ranges of 1-10. Figure 1 shows the influence of pH on the absorbance of the palladium complex at 518 nm.

As can be seen, at pH = 3.0 maximum absorbance was obtained. Hence, pH = 3.0 was chosen as the working pH and subsequent extraction was performed in acetic acid / sodium acetate buffer solution.

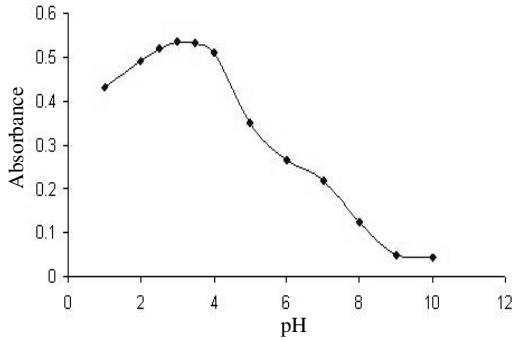

Figure 1. Effect of pH on the absorbance of complex. (*Conditions: Pd(II) 50.0 ng mL^{-1}; TMK 5.0×10^{-5} mol L^{-1}; TBA^+ 2.0×10^{-2} mol L^{-1}; $CHCl_3$ 60.0 µL and $NaClO_4$ 2.5×10^{-2} mol L^{-1}*).

Effect of TMK concentration

The effect of the concentrations of TMK on the analytical response is shown in Figure 2. The results showed that the signal increased up to a known concentration of TMK (5.0×10^{-6} mol L^{-1}), reaching plateau, which was considered as complete extraction. A concentration of 5.0×10^{-5} mol L^{-1} was chosen to account for other extractable species.

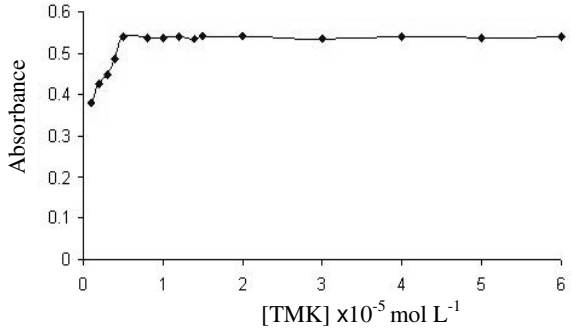

Figure 2. Effect of TMK concentration on the absorbance of the complex.

(*Conditions: Pd(II) 50.0 ng* mL^{-1}*;* TBA^+ 2.0×10^{-2} *mol* L^{-1}*;* $CHCl_3$ *60.0 µL;* $NaClO_4$ 2.5×10^{-2} *mol* L^{-1} *and pH=3.0*).

Effect of TBA^+ *concentration*

In order to investigate the optimum amount of TBA^+ on the quantitative homogeneous liquid-liquid extraction of palladium ions using TMK, the extraction of 0.5 µg of palladium from 10 mL of the sample solutions under the optimal experimental conditions was conducted by varying the concentration of TBA^+ (Figure 3).

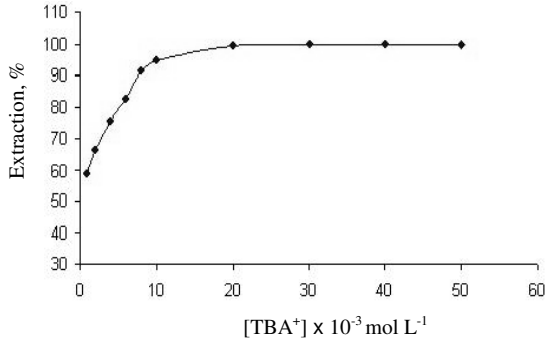

Figure 3. Effect of TBA^+ concentration on the extraction of palladium. (*Conditions: Pd(II) 50.0 ng* mL^{-1}*;* TMK 5.0×10^{-5} *mol* L^{-1}*;* $CHCl_3$ *60.0 µL;* $NaClO_4$ 2.5×10^{-2} *mol* L^{-1} *and pH=3.0*).

As can be seen, the extraction of palladium is quantitative above 2.0×10^{-2} mol L^{-1} of TBA^+. Hence, subsequent homogeneous liquid-liquid extraction experiments were carried out with 2.0×10^{-2} mol L^{-1} of TBA^+. At lower concentration, the system remains two phases and the extraction is not quantitative.

Effect of ClO_4^- *concentration*

In order to determine the concentration of ClO_4^- for quantitative recoveries, the extraction of 0.5 µg of palladium from 10 mL of the sample solutions under the optimal experimental conditions was conducted by varying the concentration of ClO_4^- (Figure 4).

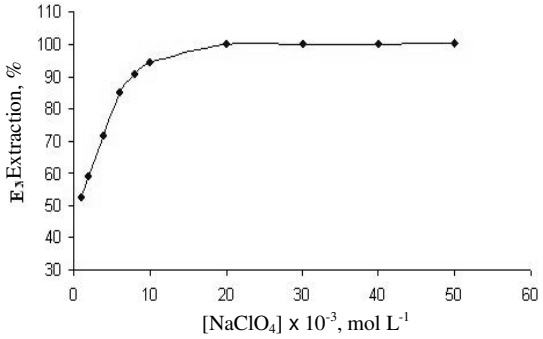

Figure 4. Effect of ClO_4^- concentration on the extraction of palladium. (*Conditions: Pd(II) 50.0 ng mL^{-1}; TMK 5.0×10^{-5} mol L^{-1}; CHCl$_3$ 60.0 µL; TBA$^+$ 2.0×10^{-2} mol L^{-1} and pH=3.0*).

As can be seen, the extraction of palladium is quantitative above 2.0×10^{-2} mol L^{-1} of ClO_4^-. Hence, subsequent homogeneous liquid-liquid extraction experiments was carried out with 2.5×10^{-2} mol L^{-1} of ClO_4^-

Effect of buffer concentration

The influence of buffer amount on extraction recovery of palladium(II) was investigated by changing concentration of the buffer and keeping other variables constant. It has been found that at buffer's concentration higher that 1.0×10^{-3} mol L^{-1} no significant variations in the extraction yield occurs. Thus, 2.0×10^{-3} mol L^{-1} concentration of buffer solution was chosen as optimal to achieve higher buffer capacity. At concentrations lower than 1.0×10^{-3} mol L^{-1}, buffer capacity was insufficient to adjust the pH

Effect of volume of chloroform

In this extraction method, the concentration factor is strongly dependent on the volume of the sedimented chloroform phase. The relationship among the volume of added chloroform and the concentration factor and extraction efficiency is shown in Figure 5.

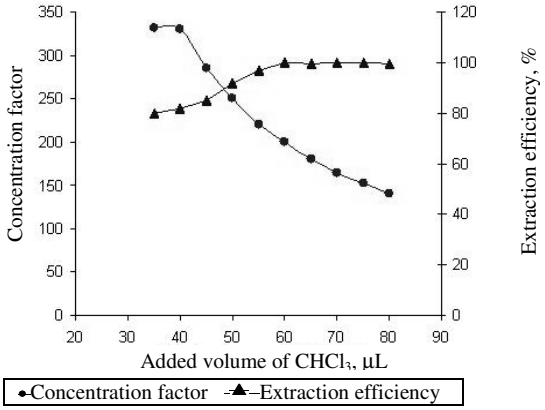

Figure 5. Effect of added volume of chloroform on the extraction of palladium and concentration factor. (*Conditions: Pd(II)50.0 ngmL^{-1}; TMK 5.0×10^{-5} mol L^{-1}; TBA$^+$ 2.0×10^{-2} mol L^{-1}; NaClO$_4$ 2.5×10^{-2} mol L^{-1} and pH = 3.0*).

As can be seen, the extraction of palladium is quantitative above 60.0 µL of $CHCl_3$. Hence, In order to achieve maximum extraction efficiency and concentration factor, 60.0 µL of added $CHCl_3$ was selected.

Selectivity of the method for palladium

For detection interferences, the influence of several ions was tested. The effect of interfering ions at different concentrations on the absorbance of a solution containing 50.0 µg L^{-1} of palladium was studied. An ion was considered to interfere when its presence produced a variation in the absorbance of the sample of more than 5%. This increment of absorbance was evaluated at wavelength 518 nm (corresponding to maximum absorption of Pd complex).

Among the interfering ions tested, Cl^-, I^-, SCN^-, NO_3^-, ClO_4^-, Li^+, K^+, Na^+, Ba^{2+}, Ca^{2+}, Mg^{2+}, Co^{2+}, Pb^{2+}, Cd^{2+}, Al^{3+}, Ni^{2+}, Sr^{2+},Fe^{2+} (Ion / Pd (II) (w/w) = 1000) and Ag^+, Fe^{3+}, Cr^{3+}, Zn^{2+}, Cd^{2+}, Cu^{2+} (Ion / Pd (II) (w/w) = 500) did not interfere at palladium determination. This is in agreement with the results reported in the literature that TMK is highly selective for palladium at pH=3±0.2[27].

Figures of merit

Table 1 summarizes the analytical characteristics of the optimized method, including linear range, limit of detection, reproducibility and concentration factor. The limit of detection, defined as $C_L = 3\ S_B / m$ (where C_L, S_B and m are the limit of detection, standard deviation of the blank and slope of the calibration graph, respectively), was 0.4 ng mL^{-1}. The relative standard deviation (RSD) for ten replicate measurements of 20.0 ng mL^{-1} Pd(II) was 2.3%.

Table 1. Analytical characteristics of proposed method.

Parameter	Analytical feature
Linear range, ng mL^{-1}	2-100
Limit of detection, ng mL^{-1}, n =10	0.4
Repeatability, RSD[a], %, n =10	2.3
Concentration factor[b]	10

[a]Pd (II) concentration was 20.0 ng mL^{-1} for which RSD was obtained. [b]Concentration factor is the volume ratio (Va/Vs) of the aqueous phase (Va) and final volume of sedimented phase (Vs).

The concentration factor (the volume ratio (Va / V*s*) of the aqueous phase (Va= 10 mL) and final volume of sedimented phase (Vs = 1.0 mL) after phase separation) was 10. Certainly a preconcentration factor of 200 (50 µL of chloroform phase was obtained from 10 mL of the homogenous aqueous solution) in combination of this method with other techniques that required low volume of sample such as flow injection analysis (FIA) or graphite furnace atomic absorption spectrometry (GF AAS) can be obtained. Preconcentration factor of 200 will make the method very promising for use at sub ng mL^{-1} level.

Application to samples

For accessing the capability of the method for real samples with different matrices containing varying amounts of diverse ions, the method was applied to separation, preconcentration and determination of palladium from 10 mL of water samples. According to the results, the concentration of palladium in analyzed water samples was below the LOD of the method. The suitability of the proposed method for the analysis of natural water samples was checked by spiking samples with 10 and 20 µg L^{-1} of palladium. Good recoveries

(98-102%) were achieved for all analyzed samples. The data obtained with the proposed method were presented in Table 2. The results indicate that the proposed method can be reliably used for the determination of palladium in various matrices.

Table 2. Determination of Pd(II) in different water samples.

Sample	Pd^{2+} spiked, ng mL^{-1}	Pd^{2+} detected, ng mL^{-1}	Recovery, %
Sample 1[a]	10.0	9.9 (2.5) [f]	99
	20.0	19.7 (2.3)	98.5
Sample 2[b]	10.0	10.0 (2.4)	100
	20.0	19.9 (2.2)	99.5
Tap water [c]	0.0	n.d.	—
	10.0	10.1(2.6)	101
	20.0	19.8 (2.5)	99
Sea water [d]	0.0	n.d.	—
	10.0	9.8 (2.7)	98
	20.0	19.6 (2.8)	98
Mineral water [e]	0.0	n.d.	—
	10.0	10.2 (2.4)	102
	20.0	20.2 (2.5)	101

[a]*Double distilled water spiked with 500 µg L^{-1} of Cu^{2+}, Co^{2+}, Cd^{2+}, Fe^{3+}, Ni^{2+} and Cr^{3+} and 1000 µg L^{-1} of K^{+} and Li^{+} ions*
[b]*Double distilled water spiked with 250 µg L^{-1} of Cu^{2+}, Co^{2+}, Cd^{2+}, Fe^{3+}, Ni^{2+} and Cr^{3+} and 500 µg L^{-1} K^{+} and Li^{+} ions.*
[c]*From drinking water system of Tehran.* [d]*Caspian sea water.* [e]*From Abali mineral water.*
[f] *RSD of three replicate experiments, n.d. = Not detected.*

Conclusions

In this work, we used a homogenous liquid–liquid extraction method for separation and determination of palladium that utilizes an ion-pair formation of TBA^{+} and ClO_4^{-} for phase separation phenomenon (a pH independent phase separation) from the homogeneous solution. This method is simple, rapid, highly selective and sensitive. High preconcentration factor can be obtained easily by this method. The proposed method can be applied to environmental and / or other sample having Pd levels higher than the detection limit of the method.

Acknowledgement

The author thanks the research council at the University of Tehran and Iran University of Science and Technology for financial support.

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