Simplified Cloud Point Extraction-Flame Atomic Absorption Spectrometry for the Preconcentration/Analysis of Trace Palladium

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In this paper, a new simplified cloud point extraction for trace palladium as a prior step to its determination by flame atomic absorption spectrometry has been developed. The separation of Pd(II) by cloud point extraction involves prior formation of a complex $[\text{PdCl}_4]^{2-}$ with sufficient KI to be extracted into the small volume of the Triton X-100-rich phase and yield the desired preconcentration. This procedure does not need any organic chelating agent as well as long incubation time. The parameters of extraction system were investigated in detail. At optimum conditions, the linear range of Pd(II) was 0.1-60.0 $\mu\text{g mL}^{-1}$. The correlation coefficient and the limit of detection were 0.9962 and 0.086 $\mu\text{g mL}^{-1}$ respectively. The proposed method was applied to extract trace amounts of Pd(II) in synthetic sample and palladium catalyst waste water with satisfactory results.

Key Words: Palladium, Cloud point extraction, Flame atomic absorption spectrometry.

INTRODUCTION

Palladium is used as a precious metal in jewellery and in some forms of chemical apparatus. It is also an excellent conductor of electricity and used for electrical contacts and in catalytic converters. But the concentration of palladium in environmental, geological and metallurgical materials is usually too low to be directly determined owing to insufficient sensitivity and matrix interferences^{1,2}. Therefore, the application of highly sensitive techniques, ICP-AES^{3,4}, ICP-MS^{5,6}, GF AAS^{7,8}, coupled with a separation and enrichment procedure is necessary⁹⁻¹⁴.

In this paper, a new simplified cloud point extraction for trace palladium as a prior step to its determination by flame atomic absorption spectrometry has been developed. It was based on the cloud point extraction of $[\text{PdCl}_4]^{2-}$ (which formed from the reaction between Pd(II) and KI by Triton X-100 as a surfactant. The proposed method was applied to extract trace amounts of Pd(II) in synthetic sample and palladium catalyst waste water with satisfactory results.

EXPERIMENTAL

A ZEE nit 700 (Analytik Jena, Germany) atomic absorption spectrometer, a MT-31 YAMATO Touch mixer (Yamato Scientific Co., Ltd) and pHs-25 pH meter (Shanghai Precision and Scientific Instrument) were used.

A stock standard solution of Pd(II) at a concentration of 1000 $\mu\text{g mL}^{-1}$ was used. Working standard solutions were obtained by appropriate dilution of the stock standard solution. A solution of 10 % (m/v) of Triton X-100 was obtained by dissolving 10 g Triton X-100 in water and diluting to 100 mL in a volumetric flask. 0.2 mol L⁻¹ KI solution and NaCl were used.

Britton-Robinson buffer solutions (B-R) were prepared by mixing the mixed acid (composed of 0.04 mol L⁻¹ H₃PO₄, AcOH and H₃BO₃) with 0.2 mol L⁻¹ NaOH in proportion. The buffer solutions were prepared to adjust the acidity of the system.

All reagents used were of analytical reagent grade and the solutions were prepared with distilled water unless otherwise specified.

Procedure

A solution containing Pd(II) was transferred to a 5 mL centrifuge tube with a graduation line. After adding 1 mL pH 6.0 BR buffer solution, 0.50 mL 0.2 mol L⁻¹ KI solution and 1 mL 10 % Triton X-114 solution, the solution was diluted to 5.0 mL with distilled water. Then 1 g NaCl was added to this solution, then shake evenly. The resultant solution immediately turned turbid at 50 °C temperature for 20 min. Phase separation was accelerated by centrifuging the tubes at 4000 rpm for 10 min. The aqueous phase was then separated by a syringe without cooling in an ice bath. After adding 1 mL pH 6.0 BR buffer solution, the surfactant-rich phase of this

procedure was diluted to 2 mL and was determined by flame atomic absorption spectrometry against a blank solution. The extraction efficiency of Pd(II) is the ratios of the amount of the solution after cloud point extraction to the one of the origin solution.

RESULTS AND DISCUSSION

Effect of salts on cloud point extraction efficiency: The effects of different salts on cloud point temperature and extraction efficiency of Pd(II) (E %) were studied. It was found that there is little effect of Na_2SO_4 , NaCl , NH_4Cl on E %, but E % was dramatically reduced with the increase of the concentrations of $\text{CH}_3\text{COONH}_4$ and Na_2CO_3 , the reasons could be that $\text{CH}_3\text{COONH}_4$ affected the process of phase separation and the pH of the system was altered by Na_2CO_3 . To sum up, NaCl was chosen as the additive.

Effect of pH on extraction efficiency: Cloud point extraction of Pd(II) were performed in different pH buffer solutions. The separation of Pd(II) by cloud point extraction involves prior formation of a complex $[\text{PdCl}_4]^{2-}$ with sufficient KI to be extracted into the small volume of the surfactant-rich phase, thus yielding the desired preconcentration. The extraction yield depends on the pH at which complex formation occurs. The effect of different pH values on the E % was recorded in the range of pH 2-11 (Fig. 1) and the quantitative extraction was observed in the range of pH 5-7. Therefore, pH 6 was selected in future work.

Fig. 1. Effect of pH on extraction

Effect of concentration of TritonX-100: Triton X-100 was chosen for the formation of the surfactant-rich phase due to its low cloud point temperature and high density of the surfactant-rich phase by which phase separation will be facilitated by centrifugation. Extraction of Pd(II) with the TritonX-100 concentration was investigated within the range of 0.2-4 g L⁻¹, which is shown in Fig. 2. The optimum surfactant concentration used for the Pd(II) was 2 g L⁻¹. So, the concentration of TritonX-100 was chosen as 2 g L⁻¹ in order to achieve the optimal surfactant concentration in conjunction with the highest possible extraction efficiency.

Effect of the concentration of KI: The effect of KI concentration was investigated in the range of 2×10^{-6} -0.04 mol L⁻¹. The result was shown in Fig. 3. As Fig. 3 shows the

E % for palladium in the surfactant-rich phase increased by increasing iodide concentration up to 0.005 mol L⁻¹ and remained constant at higher concentrations. By increasing iodide concentration the concentration of $[\text{PdI}_4]^{2-}$ of palladium increases and causes more extraction efficiency. So a 0.02 mol L⁻¹ KI concentration was used as optimal.

Fig. 2. Effect of Triton X-100

Fig. 3. Effect of KI

Effect of the equilibrium temperature and time: Optimal equilibration temperature and shortest time are necessary to complete reactions and to achieve easy phase separation and preconcentration as efficiently as possible. The results indicate that the experiment in the optimized reagent concentration after heating for 20 min in 50 °C and centrifuging by 10 min at 4000 rpm and cooling to room temperature lead to high recovery in short time.

Characteristics of the method: Under the optimum conditions, the calibration graph was linear in the range 0.1-60 µg mL⁻¹. The calibration equation is $A = 0.00391c \text{ (}\mu\text{g mL}^{-1}\text{)} + 0.017$, with a correlation coefficient of 0.9962. The limit of detection, defined as $DL = 3 \text{ SB/m}$, where SB and m are standard deviation of the blank and the slope of the calibration graph, respectively, was 0.086 µg mL⁻¹. The relative standard deviation was 1.8 % ($c = 5.0 \mu\text{g mL}^{-1}$, $n = 3$).

Effect of coexisting ions: The effect of foreign ions on the preconcentration of palladium by the proposed method was investigated. An ion was considered as interfering when

it caused a variation in the absorbance of the sample greater than $\pm 5\%$. Tolerance limits (ion/Pd(II) (w/w)) of interfering ions in the determination of 5 ppm Pd(II) were list in the following: Ca^{2+} , K^+ , Na^+ , Zn^{2+} , Cd^{2+} (1000); Cr^{3+} , Co^{2+} , Ni^{2+} (400); Al^{3+} (200); Fe^{3+} , Cu^{2+} (32); Pt(IV) , Au(III) , Ir(IV) (5).

Determination of Palladium in different samples: In order to validate the method for accuracy, palladium in a certified reference material (GSB 04-1743-2004, certified value: 1000.00 ± 3.4 ppm) was determined, the result was 9884 ± 2.8 ppm and the recovery was 98.8 %. There is no significant difference between the found value and the certified value for palladium. The proposed method was applied to determination of trace amounts of palladium in synthetic samples and the palladium catalyst waste water with satisfactory results (Table-1).

TABLE-1
DETERMINATION OF Pd(II) IN SYNTHETIC SAMPLE AND
PALLADIUM CATALYST WASTE WATER (n =3)

Sample	Determined ($\mu\text{g mL}^{-1}$)	Added ($\mu\text{g mL}^{-1}$)	Found ($\mu\text{g mL}^{-1}$)	RSD (%)	Recovery (%)
Synthetic sample ^a	10.00	4.00	4.02	1.24	100.5
		8.00	7.92	0.49	99.0
		12.00	11.86	0.82	98.8
Palladium catalyst waste water	46.25	4.00	3.89	1.03	97.3
		8.00	7.89	1.21	98.6
		12.00	11.84	1.08	98.7

a: Synthetic sample contained $500.0 \mu\text{g mL}^{-1}$ of K^+ , Mg^{2+} , Co^{2+} , Mg^{2+} , Ca^{2+} , Ni^{2+} and $20 \mu\text{g mL}^{-1}$ of Pt(IV) , Ir(IV) , Au(III)

Conclusion

A simple, rapid and sensitive cloud point extraction methodology has been developed and optimized for the preconcentration of trace palladium before its determination

by flame atomic absorption spectrometry. The proposed procedure does not need any organic chelating agent, long incubation time. The proposed method can be applied to the preconcentration and determination of palladium in waste water sample.

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