Asian Journal of Chemistry; Vol. 28, No. 2 (2016), 249-252

ASIAN JOURNAL OF CHEMISTRY

http://dx.doi.org/10.14233/ajchem.2016.17895

Vortex-Assisted Liquid-Phase Microextraction for Platinum in Water Samples Prior to Flame Atomic Absorption Spectrometry Determination

BOYANG XING[1], YALING YANG[2,3,*] and LIYAN QIAN[4]

[1]Automation Research and Design Institute of Metallurgical Industry, Beijing 100071, R.P. China
[2]Faculty of Life Science and Technology, Kunming University of Science and Technology, Kunming 650500, Yunnan Province, P.R. China
[3]Yunnan Metallurgy Group Co. Ltd., Kunming 650031,Yunnan Province, P.R. China
[4]Yunnan Environmental Monitoring Center, Kunming 650034, Yunnan Province, P.R. China

*Corresponding author: E-mail: yilyil8@163.com

Received: 26 April 2015; *Accepted*: 14 July 2015; *Published online*: 3 November 2015; AJC-17584

A vortex-assisted liquid-phase microextraction was applied for the extraction of trace amounts of platinum(II) prior to flame atomic absorption spectrometry detection in the water sample. Ammonium pyrolysine dithiocarbamate was used as the chelating agent and *n*-octanol as an extractant. The fine droplets of *n*-octanol were made and dispersed as a cloud in the aqueous sample with the help of vortex mixing. Different parameters such as the pH, the amount of ammonium pyrolysine dithiocarbamate, the composition and volume of the extraction agent and vortex time were studied to get the optimum results. Under optimal conditions, the low limit of detection is 2.0 μg mL^{-1}. Recoveries of platinum spiked into tap water samples were in the range of 85.0~91.5 %. The relative standard deviations is 2.12 % (n = 6). The correlation coefficient of the calibration curve is 0.9977. The proposed method was successfully applied for the determination of platinum in the real tap water samples.

Keywords: Vortex-assisted, Liquid-phase microextraction, Ammonium pyrolysine dithiocarbamate, Platinum, FAAS.

INTRODUCTION

Platinum is used in chemical catalysts, electrical appliances and jewellery, but the greatest increase in platinum demand has been in automotive emission control catalysts [1]. In recent years, because of sewage discharge made it a lot of emissions and produced huge environmental pollution [2]. Platinum is one of the toxic metal elements, it can dissolve in soil, water and enter the food chain at last [3]. It is carcinogenic which will harm to the human cells [4,5]. Therefore, the determination of platinum is very important. Inductively coupled plasma-atomic emission spectrometry (ICP-OES), electrothermal atomic absorption spectrometry (AAS) have been reported for the determination of trace elements in natural water [6], but the direct determination of platinum is limited because its content tends to be low and other impurity interference [7-11]. So the pretreatment of the sample before separation and extraction is very necessary. Commonly used methods are ion exchange, filtration, solid phase extraction (SPE) [12], cloud point extraction (CPE) [13] and liquid-liquid extraction (LLE) [14].

Yiantzi *et al*. [15] introduced a new microextraction method termed vortex-assisted liquid-phase microextraction (VALPME) whereby dispersion of low density extraction solvent into water is obtained through using vortex mixing, a mild emulsification procedure [16,17]. Our work is an improvement of dispersive liquid-liquid microextraction (DLLME). Unlike traditional dispersive liquid-liquid microextraction, the procedure does not need of organic dispersive solvent. The fine droplets form in which vortex-mixing play the role the stirrer bar, decreasing the extraction time and could rapidly extract target analytes from water because of the shorter diffusion distance and larger interfacial area.

In this work, the possibility of platinum enrichment by vortex-assisted liquid-phase microextraction was considered. Ammonium pyrolysine dithiocarbamate (APDC) was selected as the chelating reagent [18] and a new microextraction method combined with flame atomic absorption spectrometry (FAAS) was developed for separation, enrichment and determination of platinum in water samples. Factors affecting the extraction efficiency, such as pH, concentration of chelating reagent, extraction time and nature of the organic solvent were studied and optimized.

EXPERIMENTAL

The pH values were measured using a pHSJ-4A pH meter equipped with a glass-combination electrode (Shanghai Precision and Scientific Instrument Corp., China). A vortex

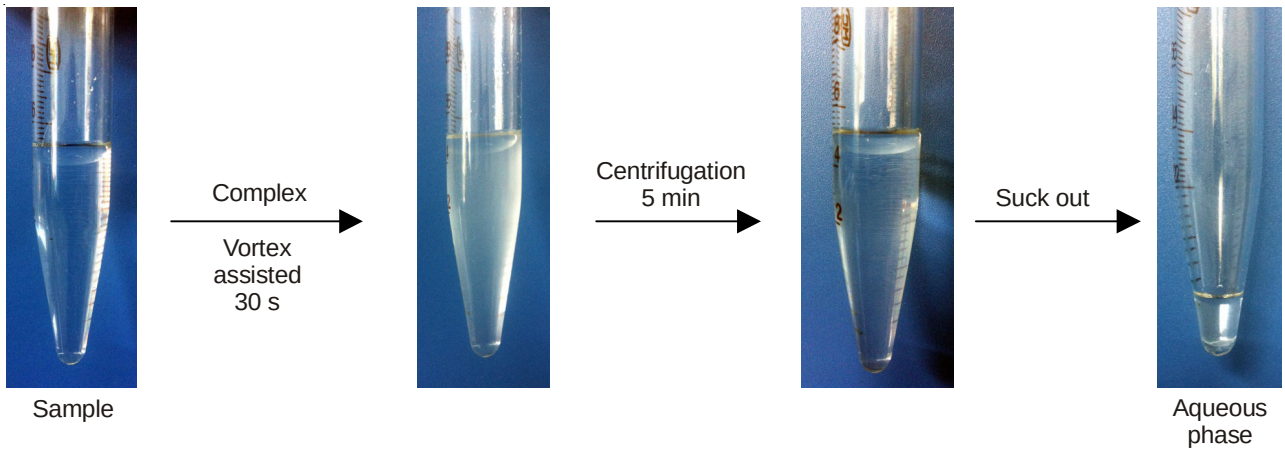

Fig. 1. Vortex-assisted liquid-phase microextraction procedure

mixer (Shanghai hanuo instrument Co. Ltd., XH-B, Shanghai, China) was used for forming cloudy solution. Flame atomic absorption spectrometer (AA6300, Shimadzu, Japan) was used for the determination of the concentration of metal. A centrifuge (Shanghai surgical instrument factory, 80-2, Shanghai, China) was used to complete phase separation.

All the reagents used in this study were analytical grade and deionized double-distilled water was used as experimental water throughout the research. Laboratory glassware was kept overnight in a 10 % (v/v) HNO_3 solution then washed three times with deionized double-distilled water.

The stock standard solution of Pt(II) (1000 μg mL^{-1}) was obtained from the National Institute of Standard (Beijing, China). Ammonium pyrolysine dithiocarbamate solution (Shanghai, China) (10 μg mL^{-1}) was prepared by dissolving in deionized double-distilled water. The buffer solution (pH 10.0) was prepared by mixing appropriate mounts of ammonia and ammonium chloride solutions. *n*-Octanol, isobutyric acid, *n*-butyl alcohol, *n*-hexylic acid, *n*-caprylic acid, *n*-nonylic acid and isooctanol were of analytical grade and purchased from Sigma (St. Louis, Mo., USA).

Experimental procedure: Fig. 1 shows the vortex-assisted liquid-phase microextraction procedure. An aliquot of 5 mL aqueous solution containing 10 μg mL^{-1} of Pt(II) with adjusted to pH 4 with buffer, was placed in a 10 mL vial. After addition of 100 μL containing 10 μg mL^{-1} of ammonium pyrolysine dithiocarbamate solution, 400 μL of *n*-octanol or isooctanol was added in and diluted to 5 mL then vortex-mixed for 50 s. A cloudy solution, resulting from the dispersion of fine *n*-octanol or isooctanol droplets in the aqueous solution, was formed in the test tube. Then the turbid was centrifuged for 5 min at 3500 rpm leading to aggregation of *n*-octanol or isooctanol as a floating drop on the surface of solution. The aqueous phase was then carefully removed by using a syringe with a long needle. And *n*-octanol or isooctanol phase was diluted with methanol solution to 1.0 mL and determined by flame atomic absorption spectrometry.

RESULTS AND DISCUSSION

Effect of pH: pH is very important to metal chelate formation and microextraction. The range of pH values is from 3 to 9. Fig. 2 shows the effect of pH on the recoveries for platinum. The experiments show that the recovery is highest in pH 4. So the pH 4 was selected as optimum pH in the subsequent study.

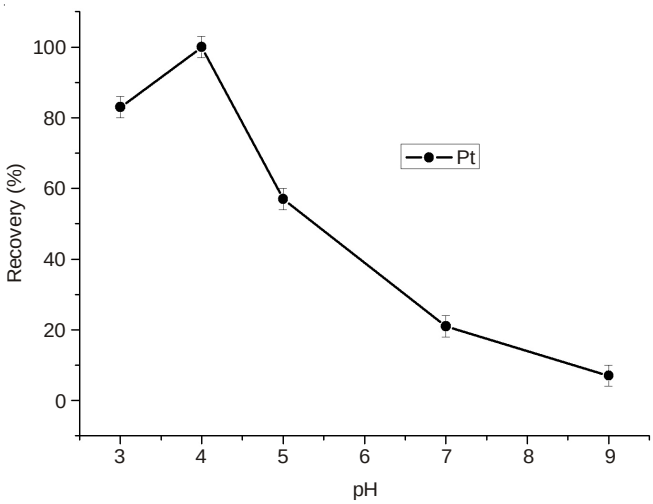

Fig. 2. Effect of pH

Effect of ammonium pyrolysine dithiocarbamate concentration: The effect of ammonium pyrolysine dithiocarbamate concentration on the extraction efficiency was evaluated in the range of 40-140 μg mL^{-1}. The results are shown in Fig. 3, with the increasing concentration of ammonium pyrolysine dithiocarbamate, the recovery increase gradually. When the concentration of ammonium pyrolysine dithiocarbamate is 100 μg mL^{-1}, the optimal recovery is found. Therefore, 100 μg mL^{-1} ammonium pyrolysine dithiocarbamate is chosen for the further studies.

Selection of extraction solvent: The extraction solvent for vortex-assisted liquid-phase microextraction should be able to form a cloudy solution in the aqueous phase. In addition it must have a lower density than water, high extraction capability for the compounds of interest, low volatility and low water solubility. Seven types extraction solvent including *n*-octanol, isobutyric acid, *n*-butyl alcohol, *n*-hexylic acid, *n*-caprylic acid, *n*-nonylic acid and is *n*-octanol were investigated. *n*-Octanol was selected because of its sensitivity, stability, lower price, low water solubility and low vapour pressure. It was also found to have the best extraction efficiency as shown in Table-1.

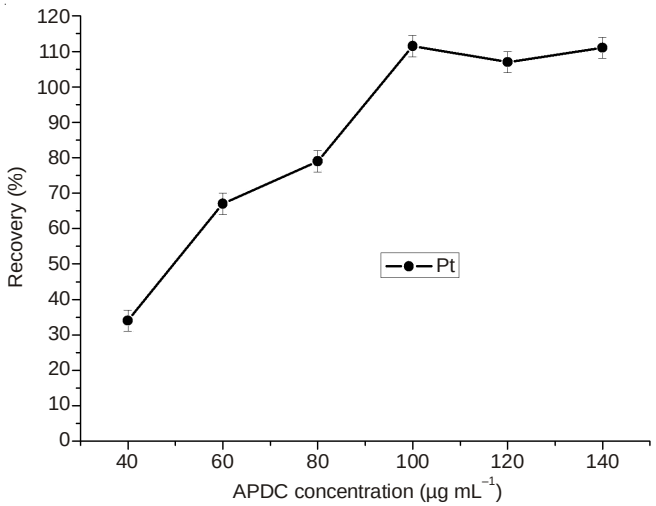

Fig. 3. Effect of ammonium pyrolysine dithiocarbamate (APDC) concentration

TABLE-1
EFFECT OF THE TYPES OF EXTRACTION SOLVENT

Types of a the extraction solvent	Recovery (%)
n-Octanol	93.0
Isooctanol	52.0
Isobutyric acid	–
n-Butyl alcohol	–
n-Hexylic acid	53.0
n-Caprylic acid	49.3
n-Nonylic acid	61.6

Effect of volume of extraction solvent: During vortex-assisted liquid-phase microextraction process, extraction solvent volume was an essential factor which could influence the occurrence of the cloudy state and also determine enrichment performance. The extraction solvent volume on the extraction efficiency was evaluated in the range of 0.2-1.0 mL. The results are shown in Fig. 4. As can be seen, the recovery keeps in a relatively high level after the volume of the *n*-octanol more than 0.4 mL. So, 0.4 mL *n*-octanol was chosen.

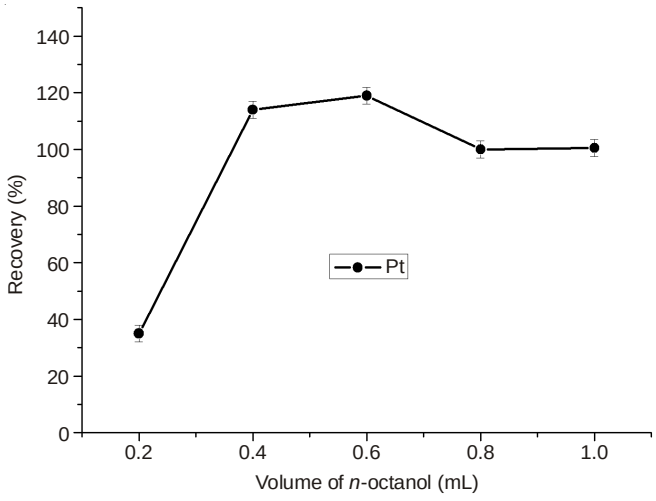

Fig. 4. Effect of the volume of extraction solvent

Effect of time assisted extraction: Emulsification is very important to microextraction process since it can increase the contact area between extraction solvent and complex. Three ways to emulsifying related to vortex-assisted, hand-assisted and ultrasonic-assisted. And times three ways of assisted extraction were tested in the range of 20-80 s. The results are shown in Fig. 5. It was seen that vortex-assisted achieve optimal extraction efficiency at 60 s.

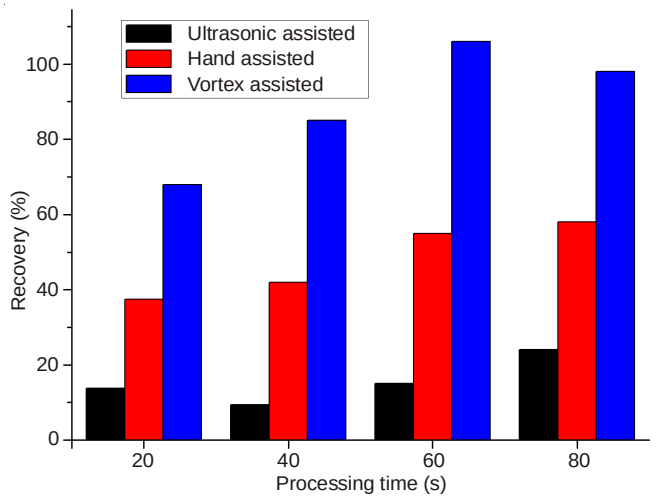

Fig. 5. Effect of the way and time assisted extraction

Effect of foreign ions: The effect of other ions in the extraction of platinum was studied under optimized conditions. Because cations may react with ammonium pyrolysine dithiocarbamate and lead to the decrease of extraction efficiency, 10 mL of sample solution containing platinum and other ions were prepared and treated with the developed procedure. The tolerance limit was defined as the foreign ion concentration causing a change in the absorbance of less than ± 5 % (Table-2).

TABLE-2
TOLERANCE LIMITS FOR IONS INTERFERING WITH THE DETERMINATION OF 20 μg L^{-1}

Ions	Interfering ion to analyte ratio
Cl^-, NO^{3-}, SO_4^{2-}, Br^-, HCO_3^{3-}	1500
Ca^{2+}, Mg^{2+}, K^+, Na^+	2000
Cr^{3+}, Mn^{2+}, Zn^{2+}, Cd^{2+}, Ni^{2+}, Pb^{2+}	800
Cu^{2+}, Al^{3+}, Fe^{3+}, Fe^{2+}	750

Accuracy and applications: Under the optimized conditions, the analytical performance of the proposed method was evaluated. A calibration curve was constructed by pre-concentrating of 10 mL of sample solutions. The calibration graph was linear in the range of 10-800 μg L^{-1}. The limit of detection (LOD), defined as $C_L = 3S_B/m$ (where C_L, S_B and m are the limit of detection, standard deviation of the blank and slope of the calibration graph, respectively) is 2 μg L^{-1}. Other analytical features of the proposed method such as calibration equation, mean recovery, correlation coefficient and the relative standard deviation (RSD) were also investigated (Table-3).

Analysis of real samples: Three water samples including tap water containing 0, 10 and 20 μg mL^{-1} of platinum were analyzed by FAAS at the same day and the next day after took same treatment. And the results show in Table-4 demonstrated that the method proposed in the study can be successfully applied to the determination of platinum in real water samples.

TABLE-5
COMPARISON OF PUBLISHED PRECONCENTRATION METHODS FOR PLATINUM WITH THE PROPOSED METHOD

Method	LR (μg L^{-1})	LOD (μg L^{-1})	RSD (%)	Extraction time	Ref.
SPE-FAAS	1-10	< 3.0	< 8.00	> 1 h	[19]
CS-FAAS	4-25	< 4.0	< 2.00	> 30 min	[20]
AOLSP-EAAS	0-20	< 1.0	< 1.60	> 10 min	[8]
VALPME-FAAS	10-800	2.0	< 2.12	≤ 15 min	This work

TABLE-3
PERFORMANCE CHARACTERISTICS OF PROPOSED METHOD

Characteristics	Data
Regression equation	A = 0.001954*C-0.00011684
R^2	0.9977
LOD (μg L^{-1})	2.0
RSD (%) (n = 6)	2.12
Mean recovery (%)	87.4
Linear range (μg L^{-1})	10-800

TABLE-4
DETERMINATION OF PLATINUM IN WATER SAMPLES

Samples	Added (μg mL^{-1})	Found (μg mL^{-1})	Recovery (%)
Processing	0	–	–
	10	8.2	82.0
	20	17.5	87.5
Next day	0	–	–
	10	8.1	81.0
	20	17.0	85.0

Comparison with other methods: Determination of platinum in the aqueous samples by vortex-assisted liquid-phase microextraction compared with the other reported preconcentration methods used for determination of platinum and the results are shown in Table-5. The proposed method shows a comparatively low detection limit, short extraction time and high sensitivity.

Conclusion

In this study, liquid-phase microextraction based on vortex-assisted couple with flame atomic absorption spectrometry has been developed for separation and sensitive determination of platinum in aqueous samples. *n*-Octanol was used as extraction agent and ammonium pyrolysine dithiocarbamate as chelating reagent. Several influencing factors including selection of extracting solvent, the way assisted extraction are discussed in the article. The study is proposed as valuable tools for the microextraction of platinum from water samples, offering a simple, inexpensive and rapid alternative to conventional sample preparation methods.

ACKNOWLEDGEMENTS

The work was greatly supported by the National Natural Science Foundation of China (No. 20961012), Drug Detection and Safety Control of Innovation Team of Kunming University of Science and Technology, Analysis and Testing Foundation of Kunming University of Science and Technology (No. 2012121) and Innovation Fund for Small and Medium Technology Based Firms (No. 11C26215305936).

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