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Atomic Absorption Spectrometric Determination of Trace Amount of Rhodium by Using Ligandless Dispersive Liquid-Liquid Microextraction Based on Solidification of Floating Organic Droplet

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ABSTRACT

In this article, ligandless dispersive liquid–liquid microextraction based on the solidification of floating organic drop was used as a sample preparation method prior to flame atomic absorption determination trace amount of rhodium in standard and dust samples. Several factors that may be affected on the extraction process, such as extraction and disperser solvent, the volume of extraction and disperser solvent, effect of salt, pH of the aqueous solution and extraction time were optimized. Under the best experimental conditions, the calibration curve exhibited linearity over the range of 10.0 ng mL^{-1}- 3.7 μg $mL^{-1}$with a correlation coefficient of 0.9992 and detection limit was 1.5 ng mL^{-1} based on $3S_b$. Eight replicate determination of 1.0 μg mL^{-1} rhodium gave a mean absorbance of 0.255 with relative standard deviation of ±1.7%. Finally, the developed method was successfully applied to extraction and determination of the rhodium ions in the dust and standard samples and satisfactory results were obtained.

Key words: Dispersive liquid–liquid microextraction; Ligandless; preconcentration; Rhodium determination; Solidification

1. INTRODUCTION

Rhodium together with platinum and palladium play a decisive role in the performance of exhaust systems, worldwide applied in vehicles to reduce the emission of gaseous pollutants. However, the hot exhaust gases flowing through the converter cause abrasion of these units, leading to the emission of the metals to the environment. Although platin group elements (PGE) are used for medical purposes in dental alloys and as anti-cancer drugs, the largest part of PGE emissions originates from automobile traffic [1]. Thus, these novel anthropogenic metals have an increasing impact on nature due to the increasing number of cars equipped with catalytic converters. The monitoring of rhodium originating from the emission of the automotive catalytic converter attrition into environmental samples has paramount importance with respect to estimation of the future risk of the human health and the ecosystem. Several researches had been carried out on developing

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reliable analytical methods for accurate determinations of traces of PGEs in different materials. Most of the attention had been focused on Pt determinations. A considerable volume of data has been accumulated on low-level Pt determinations at polluted sites and trends in concentrations of Pt over a period of years. However, corresponding Rh data were mostly missing. The determination of rhodium had been studied by different techniques such as atomic absorption spectrometry (AAS) [2], spectrophotometric methods [3], inductively coupled plasma combined with optical emission spectrometry (ICP-OES) and inductively coupled plasma combined with mass spectrometry (ICP-MS) [4] in catalysts, geological, environmental and alloy samples. The direct determination of rhodium ions in complex matrices was limited due to their usually low concentrations and matrix interferences. In trace analysis, therefore, a preconcentration and separation were necessary to improve sensitivity and selectivity of determination. Ideally, an analytical separation method should be rapid, simple, and inexpensive, give quantitative recovery of analytes without loss or degradation; should yield a solution of analyte that is sufficiently concentrated to permit the final measurement to be made without the need for concentration, and generate little or no laboratory waste that has to be disposed [5].

Several procedures had been proposed and applied for the separation and determination of rhodium by atomic spectrometry based on the nature of samples, the content of analytes and the measurement techniques [2]. For many decades the most common method for performing analytical separation on complex environmental was liquid extraction. Unfortunately, liquid–liquid extractions frequently fail to meet several of the ideal criteria listed in the previous paragraph.
Recently, efforts have been directed towards miniaturization of the liquid–liquid extraction procedure by greatly reducing the amount of organic solvent, leading to the development of liquid-phase microextraction methods. Liquid-phase microextraction (LPME) was introduced by Jeannot and Cantwell in 1996[6]. Presently, it can be performed in different modes, including direct immersion liquid-phase microextraction [7], dynamic liquid-phase microextraction [8], continuous-flow LPME [9], solvent bar LPME [10], hollow fiber liquid-phase microextraction [11], headspace liquid phase microextraction [12] and dispersive liquid–liquid microextraction [13]. Of which, dispersive liquid–liquid microextraction (DLLME) is the latest one, which was introduced by Assadi and co-workers in 2006 [13]. In this method, an appropriate mixture of extraction solvent and disperser solvent were used. The surface areas between extraction solvent and sample solution are infinitely large initially because a cloudy solution could be formed. Therefore, the extraction equilibrium can reach quickly. The method has attracted much attention due to their advantages such as fast analysis, low consumption of organic solvent and simplicity [14, 15]. However, the extraction solvent is limited in the solvents, which have higher density than water, such as chlorobenzene, chloroform, tetrachloromethane and carbon disulfide, and all of them are toxic and environment-unfriendly.

A new mode of liquid-phase microextraction based on solidification of floating organic droplet (LPME-SFO) was developed [16, 17]. In this method, no specific holder, such as the needle tip of microsyringe, the hollow fiber and polychloroprene rubber (PCR) tube, is required for supporting the organic microdrop due to the using of organic solvent with low density and proper melting point. Furthermore, the extractant droplet can be collected easily by solidifying it in the lower temperature. However, the extraction time is somewhat long, thus it cannot satisfy the demand of fast analysis.
Xu and co-workers [18] combined the advantages of the two methods (DLLME and LLME-SFO) and develop a new method named dispersive liquid–liquid microextraction based on solidification of floating organic droplet (DLLME-SFO). In this method, the enormous contact area between the organic droplets and sample solution is beneficial for the fast mass transfer from the aqueous phase to the organic phase. Accordingly the analysis time is shortened greatly. Moreover, the transfer of the solidified phase from aqueous phase can be carried out easily. Recently we reported a new DLLME method to preconcentration of silver and copper without the addition of the chelating agent [19, 20].

The aim of this work is to combine ligandless-dispersive liquid–liquid microextraction (LL-DLLME) and solidification of floating organic droplet (SFO) with flame atomic absorption spectrometry (FAAS) and developing a new method as name the two methods (DLLME and LLME-SFO) and develop a new method named ligandless-dispersive liquid–liquid microextraction based on solidification of floating organic droplet (LL-DLLME-SFO) for the preconcentration of trace amount rhodium ions in dust samples. All main factors were investigated and optimized. The LL-DLLME-SFO method was evaluated by analyzing one platinum-iridium alloy and dust samples.

2.EXPERIMENTAL

2.1. Instrumentation

A SensAA GBC (Dandenong, Australia) atomic absorption spectrometer equipped with deuterium background correction and rhodium hollow cathode lamp was used for absorbance measurements at wavelength of 343.5 nm. The instrumental parameters were adjusted according to the manufacturer's recommendations. The acetylene flow rate and the burner height were adjusted in order to obtain the maximum absorbance signal, while aspirating the analyte solution. A Metrohm 692 pH meter (Herisau, Switzerland) was used for pH measurements.

2.2. Reagents and Solutions

All the solutions were prepared in de-ionized water using analytical grade reagents (Merck, Darmstadt, Germany). The laboratory glassware was kept overnight in a 1.4 mol L^{-1} HNO_3 solution. Before using, the glassware was washed with de-ionized water and dried. The stock solution of rhodium was prepared daily from Rh^{3+} standard solution 1000.0 mgL^{-1} (Merck) by serial dilution with de-ionized water. Platinum–iridium alloy was purchased from Fine Wire Company (CA, USA). The working reference solutions were obtained daily by stepwise dilution from stock solution. The solutions of alkali metal salt (1% w/v) and various metal salts (0.1% w/v) were used to study the interference of anions and cations, respectively.

2.3. LL-DLLME-SFO Procedure

All standards and samples were prepared for analysis according to the following procedure. Eight mL of each sample was placed in a screw cap glass test tube with a conic bottom. To each test tube, 1 mL of 0.2 mol L^{-1} phosphate buffer (pH 11.5) and 1 mL of 10% (w/v) NaCl were added. Then, 1 mL of ethanol containing 25.0 µL of dodecanol (DOD) was rapidly injected into each solution. As a result, cloudy solution (water, ethanol, and DOD) was formed in each test tube. In this step, rhodium hydroxide was extracted into the fine droplets of DOD.

After centrifuging at 4000 rpm for 3 min, the organic solvent droplet was floated on the surface of the aqueous solution due to the low density below water. Then, the sample vial was put into an ice bath for 5 min, at this time the floated solvent was solidified because of the low melting point (24°C). Then, the solidified solvent was transferred to a conical test tube by a small medicine spoon. The extractant in the test tube was washed by the cold water for 2 times, and the water in the vial was drawn out by syringe. The solidified organic solvent was melted quickly in the room temperature. Prior to analyzing by FAAS, the extractant was mixed with 0.5 mL of 0.5 mol L^{-1} HNO_3 in ethanol.

2.4. Sample Preparation

One platinum-iridium alloy was analyzed. To 10.0 mg of this alloy, 10 mL of aqua regia was added and the solution was evaporated. Five mL of concentrated hydrochloric acid was added to it and the solution was warmed. Then, the solution was cooled and was made to 100.0 mL with de-ionized water in a volumetric flask.

The road dust samples were collected from three different roadsides in the Kerman city in Iran. The samples were dried at 100 °C for 2 h, ground, passed through a sieve of 200 meshes and homogenized. 2.50 g of each sample was weighed into a 100 mL of beaker. In order to decompose it, 10 mL of aqua regia was added to the beaker and the mixture was heated almost to dryness. Then, 10 mL of aqua regia was added again to the residue and the mixture was evaporated to dryness. The insoluble part was filtered through a filter paper (blue band) and washed with de-ionized water. The pH was adjusted to 11 and the total volume was made up to 25.0 mL with de-ionized water in calibrated flaks.

3. RESULT AND DISCUSSION

In this study, the combination of LL-DLLME-SFO with FAAS was developed for determination trace amounts of rhodium. Several factors that may be affected the extraction process, such as type and volume of the extraction solvent, type and volume of the disperser solvent, pH and ionic strength were optimized. The optimizations were carried out on aqueous solution containing 8.0 µg of rhodium.

3.1. Selection of Type and Volume of The Extraction Solvent

Selection of the extraction solvent is crucial in the optimization of LL-DLLME-SFO conditions [18]. It should have low solubility in water, high affinity to analytes, low melting point below room temperature and lower density than water. In this work, 1-undecanol and 1-dodecanol were selected as extraction solvent, and their extraction efficiency were studied. The results were shown that both of solvent are suitable for extraction of rhodium. While the 1-undecanol is more expensive than 1-dodecanol (DOD), so DOD was selected as the extraction solvent in the subsequent experiments. Also the effect of the DOD volume on the extraction efficiency was investigated. Experiments were performed with different volumes of DOD (15.0-60.0 µL) as the extraction solvent and 1 mL of ethanol as the disperser solvent. The results were shown in Figure. 1. It was observed that the maximum extraction efficiency was obtained in the presence 20.0 to 40.0 µL of DOD. Below or above this volume range, a decrease on the extraction efficiency was observed. Therefore, 25.0 µL DOD was used as extraction solvent in the subsequent experiments.

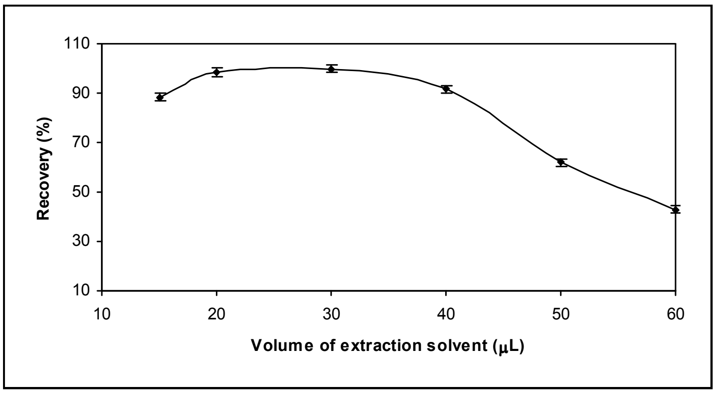

Figure1. Effect the volume of the extraction solvent (DOD) on the LL-DLLME-SFO extraction of rhodium ion. Conditions: Sample volume, 8 mL; Rh(III), 8.0 µg; Buffer, 1 mL with pH 11.5; NaCl 10%(w/v), 1 mL; ethanol, 1 mL and DOD, 25.0 µL.

3.2. Selection of Type and Volume of the Disperser Solvent

The dispersive solvent should be miscible with both water and the extraction solvent. Therefore, acetone, methanol, ethanol and tetrahydrofuran were studied. The effect of these solvents on the extraction efficiency of rhodium ions was investigated using 1.0 mL of each solvent containing 25.0 µL of DOD as the extraction solvent. The maximum extraction efficiency of rhodium ions was obtained by using ethanol as disperser solvent. Therefore, ethanol was selected for further experiments. Also, the effect of the ethanol volume on the extraction efficiency was also investigated. For investigating the effect of disperser solvent volume on extraction efficiency, various volumes of ethanol (0.5-2 mL) containing 25.0 µL DOD were used. The results were presented in Figure. 2. The results showed that the extraction efficiency increased with increasing of the volume of ethanol to 1 mL. Reduction in the extraction efficiency was observed after the volume of ethanol exceeded 1 mL. At low volume, ethanol could not disperse DOD properly and cloudy solution was not formed completely. Reversely, at high volume, the solubility of analyte in water increased by increasing of the volume of ethanol. Finally, 1 mL ethanol was chosen as the optimum volume.

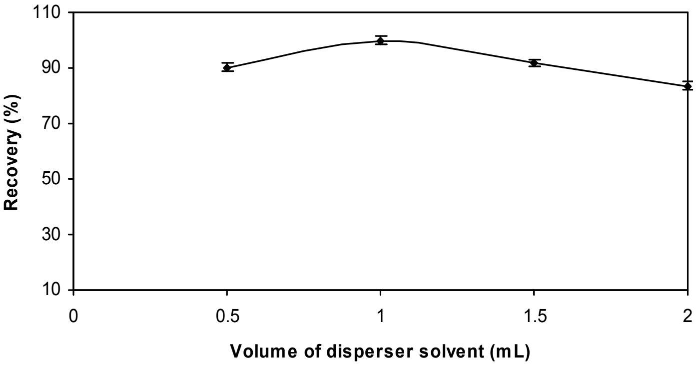

Figure 2. Effect the volume of the disperser solvent on the LL-DLLME-SFO extraction of rhodium ion. Conditions were the same as Figure. 1, except ethanol volume.

3.3. Effect of Salt

In the extraction, the solubility of many analytes in aqueous solutions decreases with increasing ionic strength due to salting out effect. Sodium chloride was used to investigate the influence of ionic strength on the extraction efficiency. For investigating the influence of the ionic strength on the LL-DLLME-SFO performance, several experiments were performed by adding varying amounts of NaCl from 0.0 to 0.2 g. The rest of the experimental conditions were kept constant. The results were presented in Figure. 3. The resulting data were shown that the maximum extraction efficiency was obtained in the presence 0.075 to 0.1 g of NaCl. Therefore, 1 mL NaCl 10% was used in all further experiments.

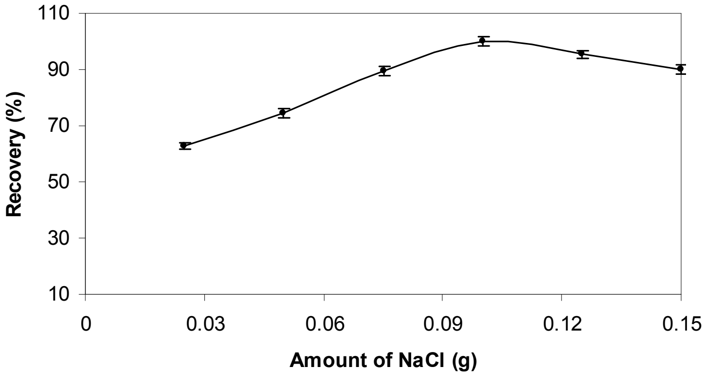

Figure 3. Effect the amount of NaCl on the LL-DLLME-SFO extraction of rhodium ion conditions were the same as Figure 1, except NaCl amounts.

3.4. Effect of Extraction Time

The extraction time was defined as interval time between the introduction of the mixture of disperser and extraction solvent and the starting of centrifuge. The effect of the extraction time was examined in the range of 0.5 to10 min with the constant experimental conditions. The obtained results showed that the extraction time was no significant influence on the extraction of rhodium ion, because of the high surface area between extraction solvent and the aqueous phase after the formation of cloudy solution, analyte diffuses into the extraction solvent quickly.

3.5. Effect of pH on LL-DLLME-SFO Procedure

The effect of pH on the extraction of rhodium was studied in the pH range of 3–12. The results were shown in Figure. 4. As can be seen, the highest extraction efficiency of rhodium was obtained at pH range of 11–12. At low pHs, the extraction efficiency didn't complete. It mean that the formation of $Rh(OH)_3$ in low pHs wasn't completed. Therefore, pH 11.5 was selected for the further experiments.

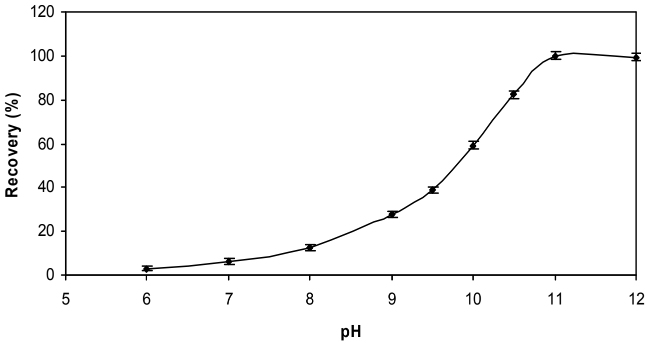

Figure 4. Effect pH of the sample solution on the LL-DLLME-SFO extraction of rhodium ion Conditions were the same as Figure. 1, except pH

3.6. Effect of Foreign Ions

In view of the high selectivity provided by flame atomic absorption spectrometry, the only interference might be attributed to the extraction step. To perform this study, various salts and metal ions were added individually to a solution containing 8.0 µg of rhodium ions and the *LL-DLLME-SFO procedure* was applied. The tolerance limit was set as the concentration of the foreign ion required to cause ±5% error. The tolerance limits of the foreign ions were shown in Table 1

Table 1. Tolerance limit of foreign ions*

Foreign ions	Foreign/Rh(III) ratio	Recovery (%)
PO_4^{3-}, $H_2PO_4^-$, HPO_4^{2-}	5000	96
CH_3COO^-	6000	103
Ca^{2+}, Mg^{2+}	3000	97
Na^+, K^+	4000	104
Pb^{2+}	1000	96
Pd^{2+}	300	95
Zn^{2+}	100	104
Mn^{2+}	500	95
Cd^{2+}	400	104
Fe^{3+}	300	103
Al^{3+}	50	95
Cu^{2+}	200	104
Ag^+	550	105
Co^{2+}	400	95
Au^{3+}	600	95
Ni^{2+}	250	105
Mo^{3+}	500	105

*Conditions were the same as Figure 1.

3.7. Analytical Performance

Performance characteristics of the method were obtained by processing standard solution of rhodium. For a sample volume of 8.0 mL, the calibration curve exhibited linearity over the range of 0.01 - 3.7 µg mL^{-1} with a correlation coefficient of 0.9992 (A= 0.2627C+ 0.0069, where *A* is the absorbance value of the eluent and *C* is the concentration of rhodium (µg mL^{-1})). Eight replicate determination of 1.0 µg mL^{-1} rhodium gave a mean absorbance of 0.255 with relative standard deviation of ±1.7%. Preconcentration of 8.0 mL of sample permitted the detection limit of 1.5 ng mL^{-1} for rhodium based on $3S_b$. The limit of quantification based on $10S_b$ for rhodium in the original solution was 5.0 ng mL^{-1}.

3.8. Analysis of Rhodium in Platinum-Iridium Alloy

The accuracy and applicability of the LL-DLLME-SFO procedure had been applied to the determination of rhodium in one platinum-iridium alloy. The results were given in Table 2. It was found that there was no significant difference between results obtained by the LL-DLLME-SFO procedure and the certified result. These results indicate the applicability of the LL-DLLME-SFO procedure for preconcentration of rhodium.

Table 2. Determination of Rh(III) in platinum-iridium alloy

Composition (%)	Certified value (%)	Found value[a] (%)
Pt, 55; Ir, 28; Pd, 3.5; Cu, 3.0; Fe, 3.5	7.0	7.12±0.36

[a] Average of three determinations±standard deviation

3.9. Analysis of Rhodium in Road Dust Samples

The LL-DLLME-SFO procedure was applied for preconcentration of rhodium in the road dust samples prior FAAS determination. The results were given in Table 3. The recovery of rhodium from the road dust samples spiked with the known amounts of rhodium ions was also studied. The results were shown in Table 3. According to these results, the added rhodium ions can be quantitatively recovered from the road dust samples by the LL-DLLME-SFO procedure. These results were demonstrated the applicability of the LL-DLLME-SFO procedure for rhodium determination in the road dust samples.

Table 3. Determination of rhodium in road dust samples

Sample	Rhodium amount ($\mu g\ g^{-1}$)		Recovery (%)
	Added	Found*	
Street dust No. 1	0.0 1.0	0.34±0.02 1.38±0.06	---- 104
Street dust No. 2	0.0 1.0	0.41±0.02 1.38±0.05	---- 97
Street dust No. 3	0.0 1. 0	0.36±0.02 1.41±0.06	---- 105

* Average of three determinations±standard deviation

4. CONCLUSIONS

In this paper, a new method is proposed for the preconcentration and determination of trace amounts of rhodium by LL-DLLME-SFO combined with FAAS. The LL-DLLME-SFO procedure does not need any chelating agent. The solidification of floating organic solvent facilitated the phase transferring. The LL-DLLME-SFO procedure has numerous advantages such as: rapidness, simplicity, low-cost, ease of operation, low toxic, high efficiency and low organic solvent-consumption. This method is suitable for the determination of trace amounts of rhodium in road dust samples. A comparison of the LL-DLLME-SFO procedure with the other reported extraction methods [5, 21-23] for rhodium extraction from water samples is given in Table 4. The obtained analytical parameters by the LL-DLLME-SFO procedure are comparable to most of those reported in the literature.

Table 4. Comparison of the LL-DLLME-SFO procedure with other reported methods for preconcentration of rhodium

System	Analysis method	Linear range (ng mL^{-1})	RSD (%)	LOD (ng mL^{-1})	Ref.
SPE	FAAS	20.0-25000.0	0.97	1.2	5
LLE	ICP-AES	-----	----	7.0	21
SPE	ICP-AES	------	4.1	50.0	22
SPE	DPP	250-7500	0.79	60	23
LL-DLLME-SFO	FAAS	10.0-3700.0	1.7	1.5	Present work

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