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Preconcentration and determination of palladium water samples by ionic liquid - dispersive liquid liquid microextraction combined with flame atomic absorption spectrometry

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A simple, rapid and efficient dispersive liquid–liquid microextraction by use of ionic liquid (IL-DLLME) method, followed by flame atomic absorption spectrometry (FAAS) was developed for the preconcentration and determination of palladium in water samples. In this method, an appropriate mixture of acetone and octyl methyl imidazolium hexafluorophosphate was injected rapidly into the aqueous sample containing palladium-DDTC complex, as a result cloudy mixture was formed. After extraction of palladium complex into fine droplet, the mixture was centrifuged. As a result, fine organic drop was setteled in the bottom of test tube. After remove of aqueous solution and dilution of organic phase; it was introduced into the flame atomic absorption by microsampler injector. Several parameters influencing the microextraction efficiency, such as the nature and volume of organic solvent, pH of aqueous solution, amount of complexing agent, stirring rate and extraction time were investigated and optimized. The applicability of technique was evaluated by determination of trace amounts of palladium in several water samples. Under the optimum conditions, the enhancement factor was 83. The limit of detection, 2.8 μgL^{-1} and relative standard deviation (RSD) 4.31 % (n=10) were obtained.

Keywords: Ionic liquid; Dispersive liquid liquid microextraction; Palladium determination; Flame Atomic Absorption Spectrometry

1. INTRODUCTION

Palladium is a metal of economic importance due to its extensive use as a hydrogenation catalyst, as a catalyst in various chemical syntheses, as a micro− contactors in electronics, in jewelry manufacture, in production of dental and medicinal devices and, in recent years, as a component in the three-way catalysts in automobile exhaust gas catalytic beads [1]. As a result of such applications, palladium can be distributed and cause damage to the environment, even at low tendency to accumulation in the food chain and low decomposition rates, palladium is grouped within the category of environmental toxins [2].

The development of analytical methods for the determination of heavy metals is important for the effective monitoring of pollution levels of this metal in the environment. Due to the very low concentration of palladium in environmental samples and the matrix interferences, the direct determination of them in environmental samples by atomic spectrometric techniques, e.g. flame and graphite furnace atomic absorption spectrometry (FAAS and GFAAS) or inductively coupled plasma-atomic emission spectrometry/ mass spectrometry (ICP-AES/MS), is usually difficult, and an initial sample pretreatment, such as preconcentration of the analyte and matrix separation, is often necessary. The quest for novel sample preparation techniques has never ceased and the demand for automation in analytical LLE combined with organic solvent reduction or elimination has led to the recent development of LPME. Recently, Asadi and co-workers developed a novel microextraction technique, termed dispersive liquid–liquid microextraction (DLLME) [3], which is based on a ternary component solvent system like homogeneous liquid–liquid extraction and cloud point extraction. Although traditional organic solvents such as CCl_4,$CHCl_3$, C_6H_5Cl, are useful as extractant phase, but to avoid environmental pollution and safety problems due to flammable and volatilization, the use of ILs has been proposed as extraction solvent. Ionic liquids (ILs), resulting from the combination of organic cations and various anions which are liquids at room temperature, have aroused increasing interest for their application in electrolytes [4] for electrochemical devices and processes and as solvents for organic synthesis [5–6]. Emerging applications include new materials production [7], solvents for separation [8] and extraction processes and as a medium for catalysis [9], as a result of their unique chemical and physical properties. ILs has negligible vapor pressure and non-flammability as well as good solubility for inorganic and organic compounds, and has been successfully applied in various areas of analytical chemistry, especially in separation sciences.

There are several literature reports for preconcentration and determination of palladium using dispersive liquid liquid microextraction [10-11], liquid-liquid extraction [12-13], hemogenious liquid liquid extraction [14] solid phase extraction [15-18] and cloud point extraction [19-20]. Despite the fact that these methods have their own advantages for application to the analysis of Pd in real samples, most of them are associated with one or more of the following disadvantages as high time consumption, solvent loss, and unsatisfactory enrichment factor. Thereby, the development of simple, rapid, selective and efficient separation and preconcentration methods for low level determination of palladium and silver is challenging area of research. Several methods of ionic liquid-based microextraction have been developed for the determination of Pb [21,22], Mn [23], Hg [24–27], Cd [28], Zn [29], V [30], Co [31], and some lanthanoids [32].

Flame atomic absorption spectrometry (FAAS) is an available technique in most laboratories and one of the most extensively used techniques for various determinations of elements with significant precision and accuracy. Nevertheless, there are often natural limitations. Typically, 1–4 mL of a sample solution is generally used for FAAS. In this work microextraction method based on ionic liquid dispersive liquid–liquid microextraction of traces Pd as diethyldithiocarbamate chelate by using 1-octyl-3-methylimidazolium hexafluorophosphate ([OMIM][PF_6]) as extraction solvent has been presented. Palladium in final volume of 120 μl was subjected to micro injection method flame atomic absorption spectrometry. Various analytical parameters including pH, amounts of sodium diethyldithiocarbamate (DDTC), amounts of [OMIM][PF_6] etc. have been optimized.

2. EXPERIMENTAL

2.1. Instrumentation

The experiments were performed using a Shimadzu atomic absorption spectrometer (AA-680) equipped with deuterium background correction. A Pd hollow cathode lamps (Hamamatsu, Photonic Co. Ltd, L233-series) operating at 244.8 nm, was used as the radiation source. The Behdad Universal Centrifuge (Tehran, Iran) equipped with a swing out rotor was used for centrifugation. All 15 ml screw cap, conical-bottom glass centrifuge tube (extraction vessel) were maintained into 0.1 mol L^{-1}, HNO_3 for cleaning of any inorganic compound and washed with distilled water. A Metrohm digital pH-meter (model Lab-827, Switzerland), equipped with a glass-combination electrode was used for pH adjustment. A Hamilton plug valve (HVP model 2-5, Cat. No. 86786, Hamilton) coupled with the nebulizer needle 1/4 in.-28UNF Hub (Cat. No. 88986, Hamilton) and the female Luer fitting (1/4 in.-28 UNF, Cat. No. 35031, Hamilton) was used for microsample introduction.

2.2. Reagents

All reagents used were of analytical grade. DDTC, ethanol, methanol,Aceton, [Omim][PF_6] and all salts used were obtained from Merck (Darmstadt, Germany). $NaPF_6$ purchased from Aldrich (Milwaukee,USA). A solution of 5×10^{-2} mol L^{-1} DDTC was daily prepared by dissolving an appropriate amount of this reagent in distilled water. The solution of [Omim][PF_6] 100 mg mL^{-1}, was prepared in acetone. A solution of 120 mg mL^{-1} $NaPF_6$ was prepared by dissolving appropriate amount of $NaPF_6$ in doubly distilled water. Stock solution of Pd^{2+} and those used for the interference study (1000 ng mL^{-1}) were prepared by dissolving appropriate amounts of their respective salts in doubly distilled water. A 2.0 mol L^{-1} acetic acid–acetate solution (Merck) adjusted to pH 6.0 by dissolution of sodium hydroxide (Merck) was employed as the buffer solution. HNO_3 and NH_3 were purchase from Merck (Darmstadt, Germany) and solutions of 0.1 $molL^{-1}$ of them were used for adjusting of pH.

2.3. Extraction procedure

An aliquot of 10.0 mL water sample or standard solutions containing Pd(II) in the range of 10.0 – 700.0 ng mL^{-1} and Na-DDTC (5.0×10^{-3} mol L^{-1}) were adjusted to pH 6 by an acetate/acetic acid buffer in a 12 mL conical-bottom glass centrifuge tube. A mixture of 50 mg of [Omim][PF_6] (extraction solvent) and 450 µL of aceton (disperser solvent) was immediately injected into the sample solution in order to induce the formation of a cloudy solution, which consisted in fine droplets of IL dispersed in the aqueous sample. The mixture was subsequently centrifuged for 5 min at 3500 rpm and the upper aqueous phase was removed with a syringe (dispersive particles of IL were sedimented at the bottom of the centrifuge tube). After this process, the IL phase (20 ± 2 µL) was dissolved in 100 µL methanol (the final volume was about 120 µL) and 100 was injected into flame atomic absorption spectrometer by micro injection method for analyses of Pd.

3. RESULTS AND DISCUSSION

In order to obtain the most effective extraction, it is important to determine the optimum DLLLME conditions for the analysis of palladium. Those conditions include the effect of different parameters such as pH, amounts of IL and disperser solvent, concentration of chelating agent, concentration of salt and coexisting ions.

3.1. Selection of ionic liquid and disperser solvent

ILs are composed of unsymmetrically substituted nitrogen containing cations (e.g. imidazole, pyrrolidine, and pyridine) with inorganic anions (e.g. Cl^-, BF_4^-, PF_6^-, and $(CF_3SO_2)_2N^-$) [31]. The IL used in DLLME must be water-immiscible. In addition, IL must be liquid in experimental conditions and have high density so that fine particles of IL can settle in aqueous solutions. Short alkyl chain imidazolium-based ILs containing Cl^-, BF_4^- and $CF_3SO_3^-$ are water-miscible and ILs containing PF_6^- and $(CF_3SO_2)_2N^-$ are water-immiscible. According to the above criteria and the cost of ILs, 1-octyl-3-methylimidazolium hexafluorophosphate ([Omim][PF_6]) was selected as extraction solvent.

For DLLME, disperser solvent should be miscible with both water and extraction solvent, therefore, acetone, methanol and ethanol were tested as disperser solvent. Under the same conditions, a series of sample solutions were studied using 500 µL of each disperser solvent and 50 mg of [Omim][PF_6]. The obtained results showed that there was no significant difference between the absorbance obtained by these solvents. Therefore acetone was selected as disperser solvent in the subsequent experiments.

3.2. Selection of the diluting agent

In the case of FAAS, the solvent should have good nebulization and burning characteristics, having no too low-boiling point and compatibility with direct injection into FAAS. Furthermore, dilution agent has to dissolve the IL and complex completely. We studied the effect of acetone methanol and ethanol in the range of 40–100%. As shown in Figure 1, in the presence of 100% methanol the solution was clear and the maximum absorbance was obtained. Therefore, methanol 100% was chosen as the diluting solvent. In the presence of 40% acetone IL-phase could not be completely dissolved, and the solution was turbid. In addition, methanol was preferred to acetone due to major compatibility of methanol with flame atomic absorption spectrometer.

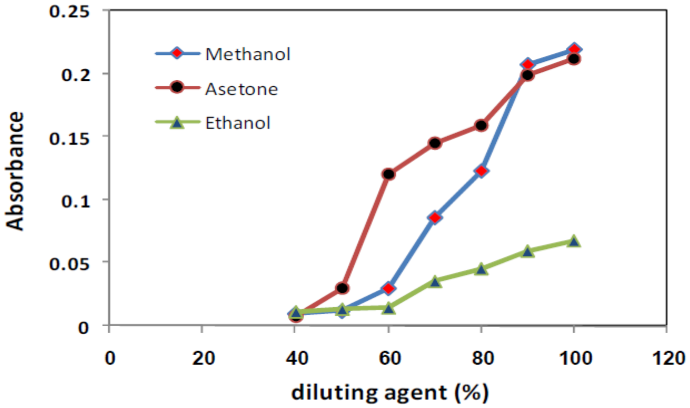

Fig. 1. Effect of diluting agent on absorption of palladium. Conditions: sample volume: 10 mL;concentration of ligand :10^{-2} mol L^{-1} ; extraction solvent amount: 50 mg; concentration of Pd: 100 µg L^{-1}; pH of solution: 6; injection volume: 500 µL.

3.3. Effect of pH and chelating agent concentration

pH plays a distinctive role on metal-chelate formation and subsequent extraction into IL phase. The effect of pH on the palladium complex extraction from water samples was studied in the range of 1.0–10.0. The results illustrated in Figure 2, reveal that the absorbance is initially increased by rising pH to 5 and then was nearly constant in the pH range of 5–10. So, pH 6 was chosen as the optimum value. The effect of concentration of DDTC was also investigated in the range of 1×10^{-6} to 5×10^{-2} mol L^{-1}. The result showed that the absorbance of Pd increased by increasing the DDTC concentration up to 1.0×10^{-3} mol L^{-1} and then remained constant up to 5×10^{-2} mol L^{-1}. A concentration of 5.0×10^{-3} mol L^{-1} of DDTC was chosen for the subsequent experiments.

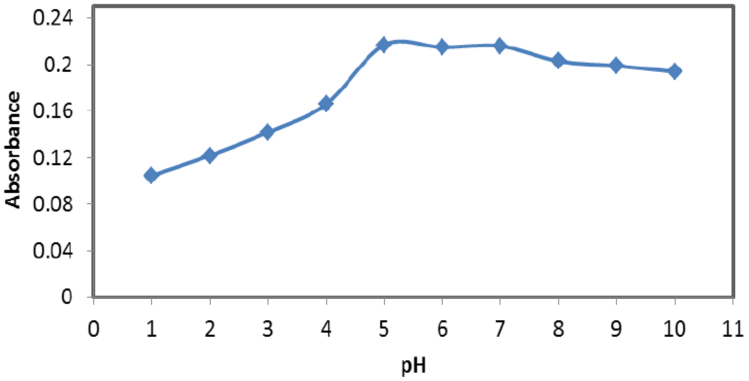

Fig. 2. Effect pH on the absorbance. Conditions: sample volume: 10 mL;concentration of ligand :10^{-2} mol L^{-1} ; extraction solvent amount: 50 mg; concentration of Pd: 100 µg L^{-1}; injection volume: 500 µL.

3.4. Effect of IL and disperser solvent

Effect of amount of [OMIM][PF_6] was studied in the range of 20–70 mg. In all studies, the amount of injection solvent (ethanol) was 500 µL. The minimum [OMIM][PF_6] amount required for the formation of cloudy solution was 30 mg. By increasing the [OMIM][PF_6] amount, the absorbance of Pd initially increased up to about 50 mg of [OMIM][PF_6] and then started to decrease (Fig. 3), which was due to an increase in the volume of settled IL-phase. Furthermore, by increasing the volume of settled IL-phase, viscosity of the IL-ethanol mixture increases. When the viscosity of solution aspirated into the flame of the atomic absorption spectrometer is high, the nebulizer uptake rate and therefore the absorbance decreases. Therefore, 50 mg of [OMIM][PF_6] was chosen as the optimum value. Since, the solubility of [OMIM][PF_6] respect to [HMIM][PF_6] and [BMIM][PF_6] in aqueous solution is very low, therefore, it is not necessary to add ion pairing agent such as $NaPF_6$.

The effect of the volume of ethanol on the extraction recovery was also studied in the range of 200 µL to 1.0 mL (Fig. 4). Using low volume of ethanol (<400 µL), the cloudy state of solution was not formed completely. At high volume of ethanol (>~700 µL), the solubility of complexes in water increased and the extraction efficiency decreased. Thereby, at high volume of ethanol the absorbance of Pd decreased. Thus, a volume of 500 µL of ethanol was used in the subsequent experiments.

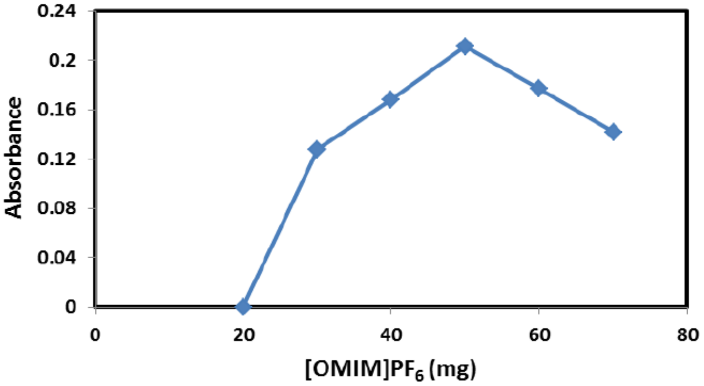

Fig. 3. Effect of amount of extraction solvent. Conditions: sample volume: 10 mL;concentration of ligand :5×10^{-3} mol L^{-1} ; pH of solution: 6; concentration of Pd: 100 µg L^{-1}; injection volume: 500 µL.

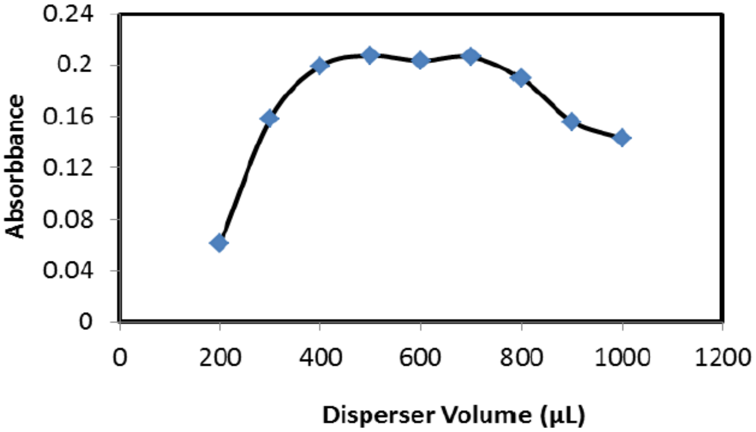

Fig. 4. Effect of disperser solvent on absorption of palladium. Conditions: sample volume: 10 mL; concentration of ligand :5×10^{-3} mol L^{-1} ; extraction solvent amount: 50 mg; pH of solution: 6 concentration of Pd: 100 µg L^{-1}; injection volume to FAAS: 100 µL.

3.7. Influence of ionic strength

To investigate the influence of ionic strength on microextraction performance, various experiments were performed by adding different amounts of $NaNO_3$ (0 – 20 %) and the rest of the experimental conditions were kept constant. As it is shown in Fig. 5, the addition of $NaNO_3$ within the interval of 0 – 16 % has no considerable affect on the extraction efficiency. But, the extraction efficiency was decreased by increasing the $NaNO_3$ concentration as a result of increasing in solubility of [OMIM][PF_6] in the aqueous phase. Moreover, at higher $NaNO_3$ concentration, the density of aqueous solution was probably become higher than that of IL, so the IL-phase did not settle at the bottom of the centrifuge tube.

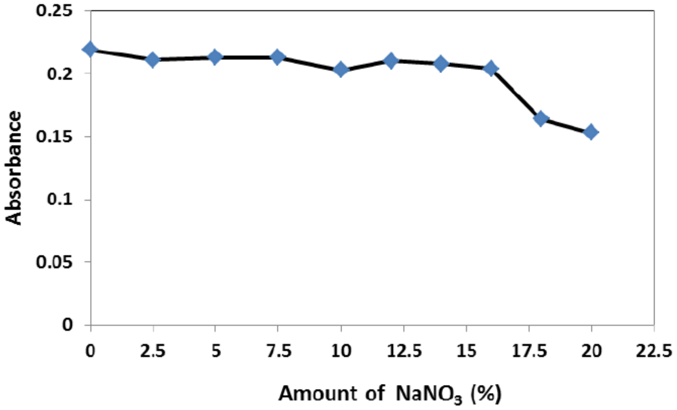

Fig. 5. Effect of ionic strength on extraction of palladium. Conditions: sample volume: 10 mL; concentration of Ligand: 5×10^{-3} mol L^{-1}; extraction solvent amount: 50 mg; concentration of Pd: 100 µg L^{-1}; injection volume 500 µL.

3.8 Effect of centrifuge conditions

A series of solutions were tested at various rates of centrifugation. The rate of centrifugation was adjusted in the range of 500–4000 rpm for 5 min. The absorbance slowly increases with increasing the rate to 3000 rpm and after that, it approximately stays constant. Therefore, 3500 rpm was selected as the best rate for centrifuging. At the optimum rate, absorbance was investigated as a function of centrifugation time. Over 4 min, the absorbance was constant, indicating complete transfer of IL phase to the bottom of the centrifuge tube, so 5 min were selected as the optimum centrifugation time.

3.9. Effect of coexisting ions

The effect of other ions in the extraction of Pd^{2+} was studied under optimized conditions. Solutions containing 20 µgL^{-1} of Pd^{2+} and different concentration of other ions were prepared and were subjected to preconcentration procedure. An ion was considered to interfere when its presence produced a variation in the absorbance of the sample of more than 5%. A1000-fold excess of alkali and alkaline earth cations (Na(I), K(I), Mg(II), Ca(II)) did not affect the Pd signal. Al(III), Mn(II), Fe(III), Cr(III), and Cd(II) did not interfere up to a concentration of 10 mgL^{-1}. Cu(II), Ni(II), Co(II), Pb(II), Ag(I), Hg(II) and Zn(II) could be tolerated up to a concentration of 1mg L^{-1}. Table 1 shows the tolerance limits of the interfering ions. This interference was eliminated using an excess of DDTC reagent in sample solutions.

Table 1. Effect of foreign ions on the preconcentration and determination of palladium.

Ions	Ion/Pd(II) (w/w)	Recovery (%)
Na^+	1000	100.4
K^+	1000	101.3
Mg^{2+}	1000	99.5
Ca^{2+}	1000	100.4
Cr^{3+}	500	98.6
Mn^{2+}	500	98.3
Fe^{2+}	500	99.5
Fe^{3+}	500	98.7
Cd^{2+}	500	97.8
Al^{3+}	500	98.1
Co^{2+}	100	97.3
Pb^{2+}	100	96.8
Ag^+	100	96.1
Cu^{2+}	100	95.9
Zn^{2+}	100	96.1
Bi^{3+}	100	96.7
Ni^{2+}	100	95.2
Hg^{2+}	100	96.1
NO_3^-	1000	101.3
SO_4^-	1000	99.1

3.10. Analysis of real sample

The proposed method was applied to several categories of samples including, tap water, ground water, river water and two synthetic samples. The results are given in Table 2. Reliability was checked either by spiking the sample. As the results showed the recovery of spiked sample is good, which suggesting the proposed procedure is reliable for the sample type examined.

Table 2. Analytical characteristics of proposed method.

Parameter	Analytical feature
Linear range, µg L^{-1}	10 - 700
Limit of detection, µg L^{-1}, n =10	2.80
Repeatability, RSD, %, n =10	4.31
preconcentration factor	83

3.11. Analytical performance

Under the optimum condition, the calibration graph was constructed by processing standard solutions of palladium according to the given procedure. The linear concentration range was 10–700 µgL^{-1} with a correlation coefficient of 0.993. The calibration function was $Y = 1.715\ X + 0.021$, where Y is the peak height and C is the concentration of palladium in µgL^{-1}. The precision of the method was studied by processing ten replicate solutions at the same day. The relative standard deviation for 50 µgL^{-1} palladium was 4.31%. The limit of detection and quantification based on $3S_b/m$ and 10Sb/m, (where S_b is standard deviation of the blank signals and m is the slope of calibration curve after extraction) was 2.80 µgL^{-1}, respectively. The enhancement factor was 83, calculated from the volume ratio of (V_a/V_s) of the aqueous phase (V_a) and final volume of sedimented phase (V_s). The analytical characteristics of the method are summarized in Table 3.

Table 3. Determination of Pd(II) in different water samples.

Sample	**Pd^{2+} spiked μg mL^{-1}**	**Pd^{2+} founded μg mL^{-1}**	**Recovery, %**
Tap water[a]	0.0	n.d.	-
	50.0	47.1(2.1)[f]	94.3
	100.0	95.1(2.3)	95.2
Well water[b]	0.0	n.d.	-
	50.0	47.8(2.6)	95.7
	100.0	96.3(2.2)	96.4
Mineral water[c]	0.0	n.d.	-
	50.0	48.9(2.3)	96.8
	100.0	97.7(2.4)	97.1
Sample 1[d]	20.0	19.7(2.5)	98.5
	40.0	39.3(2.2)	98.2
Sample 2[e]	20.0	19.4(2.7)	97.0
	40.0	39.1(2.6)	97.7

[a] From drinking water system of Tehran,[b] From Ialamic Azad University - Arak well water, [c] From Abali mineral water

[d] Double distilled water spiked with 500 μg L-1 of Cu^{2+},Co^{2+}, Zn^{2+}, Fe^{3+}, Ni^{2+} and Bi^{3+} and1000 μg L^{-1} of K^{+} and Na^{+} ions

[e] Double distilled water spiked with 250 μg L-1 of Pd^{2+}, Al^{3+}, Cd^{2+}, Fe^{2+}, Hg^{2+} and Cr^{3+} and 500 μg L^{-1} Mg^{2+} and Ca^{2+} ions.

[f] RSD of three replicate experiments, n.d. = Not detected.

4. CONCLUSION

In this work, the use of ionic liquid dispersive liquid–liquid microextraction as an alternative to other techniques of separation and preconcentration offers several advantages, including low cost, good safety, and high capacity for preconcentration of palladium with a high recovery and very good extraction efficiency.

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