Desalination and Water Treatment
www.deswater.com

doi: 10.1080/19443994.2015.1124054

57 (2016) 21634–21644
September

Taylor & Francis
Taylor & Francis Group

Development of a solvent extraction system with 4-heptylaminopyridine for the selective separation of palladium(II) from synthetic mixtures, catalysts and water samples

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Received 20 April 2015; Accepted 12 November 2015

ABSTRACT

A newly reported chelating agent, 4-heptylaminopyridine has been used for selective extraction and separation of palladium(II) from salicylate media at pH 0.5 is studied. The effect of different parameters such as pH, weak organic acid concentration, extractant concentration, equilibrium time, diluents, and stripping agent has been evaluated. Successful stripping of palladium(II) from the loaded organic phase is achieved with 6.0 M ammonia (2 × 10 mL) solution. The method affords separation of palladium(II) from binary and ternary mixtures and is applicable to the analysis of synthetic mixtures, alloys, catalysts, and water samples. The method is simple, selective, cost effective, and reproducible.

Keywords: Solvent extraction; Palladium(II); 4-Heptylaminopyridine; Water samples

1. Introduction

Platinum group metals (PGMs) are of great practical importance and they have a wide range of industrial applications, e.g. as Catalysts in organic processes, value-added components in metal alloys and the vehicle catalytic converter system. They are used in the chemical, pharmaceutical, petroleum, electronic industries, and jewelry making. These wide applications of PGMs, especially palladium(II), have increased the palladium demand by 3.5% in 2007 to a total of 6.84 million ounces, whereas the natural resources are limited [1,2]. The use of palladium and platinum as catalyst in the catalytic converters of cars and their eventual spread in the environment and also the accumulation in wastewater by rain intensified environmental concerns. Since palladium has no known biological role, all palladium compounds should be regarded as highly toxic [3] similarly, palladium(II) can bind to thiol containing amino acids, proteins, DNA, and several biomolecules and adversely affect the cellular processes [4]. Therefore, the palladium(II) is strictly limited to be 5–10 ppm level by the European Agency for the Evaluation of Medicinal products [5]. The effective palladium(II) extraction and recovery from both natural ore and industrial waste are quite important from the

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viewpoint of full utilization of resources. Therefore, the most important reasons for palladium(II) ions extraction, separation, and recovery are the environmental concerns and economical impact.

Many analytical methods have been developed to determine the presence of palladium(II) ions in clinical, environmental, industrial, and pharmaceutical samples such as spectrophotometry, atomic absorption spectrometry, solid phase micro extraction, high performance liquid chromatography, X-ray fluorescence, electrochemical methods, Inductively Coupled Plasma-Atomic Emission Spectrometry (ICP-AES) [6–11]. However, many of these are limited by instrumentation cost, high training requirements, being cumbersome, time consuming and unsuitable, especially in developing or less developed countries [12–14]. From the viewpoint of analytical chemistry, there is increasing demand to develop reliable, selective, sensitive methods to extract and separate the palladium(II) ions. Solvent extraction also called liquid–liquid extraction is a process which allows separation of two or more components, e.g. metal ions making use of their unequal solubilities in two immiscible liquid phases. The solvent extraction is a suitable method for the removal of PGMs from low concentrated sources, because it offers a number of advantages like high selectivity and metal purity. Besides, more efficient removal of metals is possible by the use of a multistage extraction. Traditionally, the hydrometallurgical recovery of PGMs is based on solvent extraction processes based on the fact that noble metal ions can easily form species which are extractable into the organic phase with various reagents [15,16]. A variety of extractants have been studied and proposed, including 2-octylaminopyridine [17], alamine 300 [18], tri-octyl/decyl ammonium chloride (Aliquat 336) [19], thiosemicarbazone derivatives [20,21], LIX 84I [22], cyanamides [23], ketones [24], alamine 336 [25], cyanex 471X [26], cyphos IL104 [27], hydroxyoximes and ketoximes [28–31], dialkyl sulfides and sulfoxide [32–35], alkyl derivative of 8-hydroxyquinoline [36], hydrophobic amines and quaternary ammonium salts [37–42], phosphonium [43], 1,2-bis(2-methoxyethylthio) benzene [44]. Extraction of palladium(II) by N-n-octylaniline [45,46] and 2-OAP [17] is reported. There is no report on the extraction and separation of palladium (II) from salicylate medium by 4-heptylaminopyridine (4-HAP). The superiority of the presently employed method is also shown in comparison with other reported methods (Table 1).

The aim of the present work is to develop a simple, efficient, and environmentally friendly extraction process for the separation and recovery of palladium (II) from salicylate medium. The effect of pertinent parameters including pH, weak organic acid concentration, extractant concentration, time, diluents, stripping agents, and diverse ions as well as binary and ternary separation on palladium(II) extraction have been investigated to obtain the optimum extraction conditions.

2. Experimental

UV/vis Spectrophotometer model-Optizen α (mecasys Co., Ltd/made in South Korea) with 1 cm quartz cell was used for absorbance measurements and pH measurements were carried out with an Elico Digital pH meter Model Li-120 with a combined glass electrode.

A stock solution of palladium(II) was prepared by dissolving appropriate amounts of analytical grade palladium chloride hydrate (Johnson Matthey, UK) in analar hydrochloric acid (1 M) and diluting to 250 mL with distilled water. 4-HAP was synthesized by reacting 4-aminopyridine with 1-bromoheptane in the presence of base sodium amide ($NaNH_2$) in dry THF [47] and its solutions were prepared in xylene. All the chemicals used were of analytical reagent grade, were supplied from Sigma (St. Loius, MO, USA). Doubly-distilled water was used throughout.

In all the extraction studies, aqueous (Pd(II) ion in appropriate concentration and 0.04 M sodium salicylate, pH was adjusted to 0.5) and organic (0.05 M 4-HAP in xylene) phases in a ratio of 2.5:1 were shaken at room temperature in glass stoppered separating funnel for 5 min. After phase disengagement, the aqueous phase was separated, and loaded organic phase was stripped with 6.0 M ammonia (2 × 10 mL). The concentration of palladium(II) from stripped solution was determined spectrophotometrically using pyrimidine-2-thiol [48].

3. Results and discussion

3.1. Effect of pH

The effect of the pH in the range 0.1–10 on the extraction of palladium(II) was carried out using 0.05 M 4-HAP in xylene. The amount of palladium(II) taken is 200 μg and aqueous–organic volume ratio of 2.5:1 was maintained. As can be seen in Fig. 1, as the pH increases from 0.3 to 1.0, the percentage extraction increases. As the pH increases above 1.0, the percentage of extraction decreases. This is because of the ion-pair complex may be less stable at higher pH. Therefore, pH 0.5 was selected for the further study.

Table 1
Comparison of the present method with earlier reported solvent extraction methods for extraction of palladium(II)

Extractant	Solvent	Acidity/pH	Stripping agent	Determination method	Equilibrium time	Refs.
LIX 84I	Dodecane	0.1 M HCl	1 M HCl	ICP-AES	120 min	[22]
Ketones	Nitrobenzene	2 M HCl	Thiourea	ICP-AES	120 min	[24]
N-n-Octylaniline	Xylene	1.0 M HCl	1:1 NH_3	Spectrophotometry	1.0 min	[45]
Dibutyl sulfoxide	Kerosene	1 M HCl	3% NH_4Cl	AAS	30 min	[34]
Alamine 300	Kerosene	7.5 M HCl	0.01 M $(NH_2)_2$ CS & 0.5 M HCl	ICP-AES	30 min	[18]
1,2-bis(2-methoxy ethylthio) benzene	Chloroform	6.02 M HCl	$(NH_4)_2SO_3$	ICP-OES	–	[44]
Phosphonium	Toluene	0.1 M HCl	0.5 M NH_4OH	ICP-AES	10 min	[43]
Aliquat 336	Kerosene	1–10 M HCl	$(NH_2)_2CS$ & HCl	AAS	12 h	[19]
Thiosemi -carbazone	Methyl *iso*butyl ketone	5 M H_2SO_4	–	FAAS	10 min	[20]
4-HAP	Xylene	0.04 M Sodium Salicylate pH 0.5	6 M NH_3	Spectrophotometry	5 min	P.M

Note: P.M = Present method.

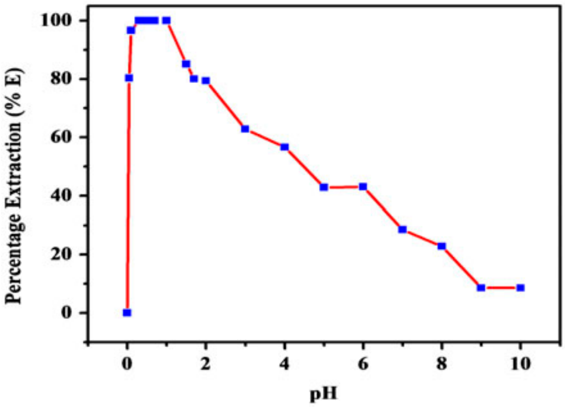

Fig. 1. Effect of pH on extraction of palladium(II).
Notes: Condition: Pd(II) 200 µg, sodium salicylate = 0.04 M, aq.:org. = 2.5:1, 4-HAP = 0.05 M in xylene, equilibrium time = 5.0 min, strippant = 6.0 M ammonia.

3.2. Effect of 4-HAP concentration on extraction of palladium(II)

The extraction behavior of palladium(II) was studied with an extractant 4-HAP concentration range of 0.01–0.15 M, at a pH of 0.5, and with 0.04 M sodium salicylate. The quantitative extraction of palladium(II) was achieved in the concentration range of 0.04–0.07 M 4-HAP. Further increase in concentration of 4-HAP, there was decrease in percentage extraction of palladium(II), this is because of formation of stable $RR'NH_2^+sal^-$ species in which sal^- will not be replaced by $Pd(sal)_3^-$ species. In order to ensure the complete extraction of palladium(II) from the aqueous phase, 0.05 M 4-HAP is recommended for the general extraction procedure.

3.3. Effect of weak organic acid concentration and diluents

The extraction of 200 µg of palladium(II) was carried out from different weak carboxylic acids like sodium succinate, sodium malonate, sodium ascorbate, and sodium salicylate at pH 0.5 and 0.05 M 4-HAP in xylene. It is apparent from the Table 2 that the extraction of palladium(II) reaches maximum (99.5%) with salicylate media in the concentration 0.03–0.05 M. This showed that the ion-pair complex of palladium(II) was found to be quantitative in salicylate media in the range of 0.03–0.05 M. As the concentration of sodium salicylate increases above 0.05 M, the percentage extraction of palladium(II) decreases. Therefore, 0.04 M sodium salicylate was used for further extraction processes. The extraction was incomplete in sodium succinate (70.2%), sodium malonate (62.2%), and sodium ascorbate (28.5%) due to the lack of ion-pair formation (Table 2).

The 200 µg of palladium(II) in 0.04 M sodium salicylate at pH 0.5 was contacted with 10 mL of 0.05 M 4-HAP dissolved in different diluents. Table 1 showed the percentage extraction of palladium(II) loaded 4-HAP in different diluents. It was found that 0.05 M 4-HAP solution in carbon tetrachloride, amyl alcohol, toluene, and xylene provides quantitative extraction of palladium(II). The extraction of palladium(II) was found to be incomplete in methyl *iso*butyl ketone

Table 2
Effect of weak carboxylic acids on extraction of palladium(II)

Concentration of acid (M)	Sodium salicylate		Sodium succinate		Sodium malonate		Sodium ascorbate	
	% E^a	D^b	%E^a	D^b	%E^a	D^b	%E^a	D^b
0.005	52.0	2.70	37.7	1.51	45.4	2.07	24.0	0.78
0.01	66.0	4.85	39.1	1.60	46.8	2.19	24.8	0.82
0.02	88.2	18.68	58.0	3.45	60.2	3.78	32.2	1.18
0.03	95.7	55.63	70.2	5.88	60.2	3.78	25.1	0.83
0.035	100	∞	69.4	5.66	61.1	3.92	27.1	0.92
0.04	100	∞	67.1	5.09	62.2	4.11	28.5	0.99
0.045	100	∞	65.7	4.78	61.4	3.97	27.7	0.95
0.05	100	∞	64.5	5.54	61.7	4.02	26.2	0.88
0.06	80.0	10	59.7	3.70	58.8	3.56	27.4	0.94
0.07	61.4	3.97	70.0	5.83	81.4	10.94	23.7	0.77
0.08	40.8	1.72	50.5	2.55	74.2	7.18	22.8	0.73
0.09	20.0	0.62	55.1	3.06	54.8	3.03	21.1	0.66
0.1	5.71	0.15	52.8	2.79	53.7	2.89	19.4	0.60

[a] Percentage extraction.

[b] Distribution ratio.

Table 3
Extraction of palladium(II) with varying diluents. Pd(II) = 200 µg, pH 0.5, Sodium salicylate = 0.04 M, 4-HAP = 0.05 M, contact time = 5 min, Strippant = 6.0 M ammonia (2 × 10 mL), aq.:org. = 2.5:1

Solvents	Dielectric constant	Percentage extraction (%*E*)	Distribution ratio (*D*)
Xylene	2.30	99.9	2,497.5
Toluene	2.38	98.2	136.38
Amyl alcohol	13.90	98.5	164.16
Carbon tetrachloride	2.24	99.1	275.27
Methyl *iso*butyl ketone	13.11	88.5	19.23
n-Butyl alcohol	17.51	60.0	3.75
Kerosene	1.8	48.5	2.35
1,2-dichloroethane	1.25	45.7	2.10
Chloroform	4.81	20.0	0.625

(88.5%), n-butyl alcohol (60.0%), kerosene (48.5%), 1,2-dichloroethane (45.7%), and chloroform (20.0%). Xylene was preferred as a diluent for further extraction procedures, because it provides a quicker phase separation with high distribution of the ion-pair complex (Table 3).

3.4. Effect of contact time

The effect of contact time on extraction of palladium(II) in 0.04-M sodium salicylate medium at pH 0.5, keeping an aq:org ratio of 2.5:1 and a 4-HAP concentration of 0.05 M was examined in the range of 5 s–15 min. The extraction was found to be quantitative over the period of 4 min (Fig. 2). But to ensure the complete extraction of palladium(II), 5-min

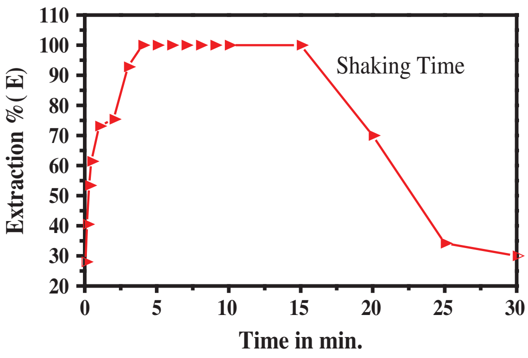

Fig. 2. Effect of contact time on extraction of palladium(II). Notes: Condition: Pd(II) 200 µg, pH 0.5, aq.:org. = 2.5:1, sodium salicylate = 0.04 M, 4-HAP = 0.05 M in xylene, strippant = 6.0 M ammonia.

Table 4
Extraction of palladium(II) with various stripping agents. Pd(II) = 200 µg, pH 0.5, Sodium salicylate = 0.04 M, 4-HAP = 0.05 M in xylene, contact time = 5 min, aq.:org. = 2.5:1

Stripping agents	Percentage extraction (%*E*)	Distribution ratio (*D*)
HCl (1–10 M)	62.7	4.20
Water	10.2	0.28
Ammonia (4–10 M)	99.9	2,497.5
H_2SO_4 (1–5 M)	6.0	0.15
HNO_3 (1–5 M)	–	0.0
Acetic acid (1–10 M)	12.6	0.36
Acetate buffer (pH 4.7)	35.4	1.36
Ammonia buffer (pH 10)	99.7	830.83
NaOH (0.1–0.3 M)	13.3	0.38

equilibration time was recommended. However, a prolonged shaking period doesn't have any adverse effect on the extraction.

3.5. Stripping of palladium(II) from the loaded organic phase

Stripping of palladium(II) was carried out using different stripping reagents. Stripping is the reverse of extraction. When the extraction of metal is carried out from acidic medium, then back extraction is generally possible from the basic medium in order to dissociate the ion-pair complex. The most efficient stripping of palladium(II) from loaded organic phase was achieved with 4–10 M ammonia and ammonia buffer pH 10. Among these two, ammonia solution is more preferred than ammonia buffer (pH 10) solution to evaporate the aqueous phase more easily. The results obtained for various stripping reagents examined are presented in (Table 4).

3.6. Loading capacity of the 4-HAP

Loading capacity of 4-HAP in xylene was determined by contacting palladium(II) in 0.04 M sodium salicylate at a fixed aqueous to organic phase ratio 2.5:1. After equilibrium and phase separation, the same organic phase was used again for the extraction of fresh feed solution of definite amount concentration of palladium(II). The extraction of palladium(II) repeated till no further extraction was found in the organic phase. The concentration of palladium(II) in the organic phase of 4-HAP was found to be 2 mg.

3.7. Effect of aqueous to organic volume ratio

In order to obtain a reliable, reproducible results and for a high extraction efficiency, the aqueous:organic volume ratio is an another important parameter in liquid–liquid extraction. The results of contacting different volume ratios of aqueous to organic phases have been studied. The results indicate that a preferred aqueous/organic (A/O) phase ratio in this study was found to be 4:1 or less. This is evident from the sharp increase in the separation efficiency as well as the distribution of palladium(II) when the phase ratio (A/O) changed from 25:1 to 4:1. This may simply be due to unavailability of reagent for the extraction at higher phase ratio, so a crowding effect occurs at a low phase ratio. However, in the recommended procedure the phase ratio is maintained at 2.5:1 so as to avoid the large consumption of sodium salicylate.

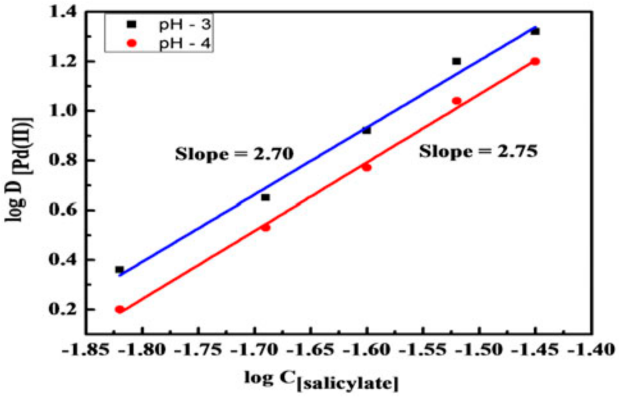

Fig. 3. Log-Log plot of log $D_{[Pd(II)]}$ vs. log $C_{[(4\text{-}HAP)]}$.
Notes: Condition: (A) Pd(II) 200 µg, pH 2, aq.:org. = 2.5:1, sodium salicylate = 0.04 M, equilibrium time = 5.0 min, strippant = 6.0 M ammonia. (B) Pd(II) 200 µg, pH 3, aq.: org. = 2.5:1, sodium salicylate = 0.04 M, equilibrium time = 5.0 min, strippant = 6.0 M ammonia.

3.8. Stoichiometry of the ion-pair complex

The probable composition of extracted species was ascertained by the slope ratio method by plotting the

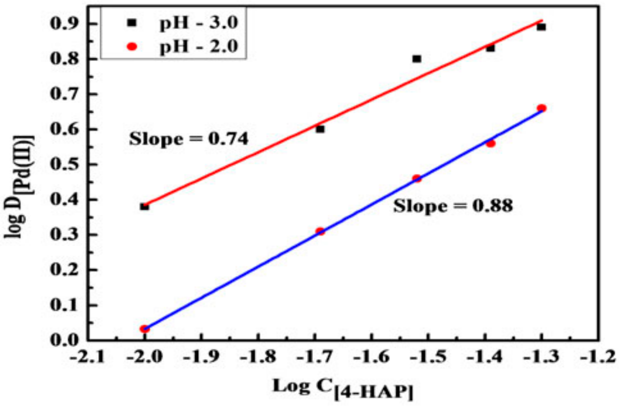

Fig. 4. Log-Log plot of log $D_{[Pd(II)]}$ vs. log $C_{[(salicylate)]}$.
Notes: Condition: (A) Pd(II) 200 µg, pH 3, aq.:org. = 2.5:1, 4-HAP = 0.05 M in xylene, equilibrium time = 5.0 min, strippant = 6.0 M ammonia. (B) Pd(II) 200 µg, pH 4, aq.: org. = 2.5:1, 4-HAP = 0.05 M in xylene, equilibrium time = 5.0 min, strippant = 6.0 M ammonia.

graph of log $D_{[Pd(II)]}$ against log $C_{[(4\text{-}HAP)]}$ at a fixed sodium salicylate concentration (0.04 M). The plots were linear, having slopes of 0.86 and 0.74, respectively, at pH 2 and 3 (Fig. 3). Also, plots of log $D_{[Pd(II)]}$ against log $C_{[(Salicylate)]}$ at a fixed 4-HAP concentration (0.05 M) were linear with slopes of 2.70 and 2.75, respectively, at pH 3 and 4 (Fig. 4). Hence, the probable composition of the extracted species was calculated to be 1:1:3 (metal:extractant:acid).

The mechanism of the extraction of species was observed to be initiated through protonation of 4-HAP to form the cationic species as $RR'NH_2^+$, while anionic species were formed by combining salicylate with palladium(II) as $[Pd(Sal)_3]^-_{aq}$ and both of these anionic and cationic species to form an ion-pair of type $[RR'NH_2^+Pd(Sal)_3^-]_{org}$.

[I] Mechanism of extraction:

$$RR'NH_{org} + H^+_{aq} \rightleftharpoons RR'NH_2^+$$

$$PdCl_{2\,aq} + Cl^-_{aq} \rightleftharpoons PdCl^-_{3\,aq}$$

$$PdCl^-_{3\,aq} + 3\,Hsal_{aq} \rightleftharpoons [Pd(sal)_3]^-_{aq} + 3\,H^+$$

$$RR'NH^+_{2\,org} + [Pd(sal)_3]^-_{aq} \rightleftharpoons [RR'NH_2^+\,Pd(sal)_3^-]_{org}$$

[II] Mechanism of stripping:

When organic phase was back stripped with 6.0 M NH_3 solution, there is formation of $[Pd(NH_3)_2(H_2O)_2]^{2+}$ species in the stripped solution [55]:

$$[RR'NH_2^+\,Pd(sal)_3^-]_{org} + 2\,NH_4OH \rightleftharpoons RR'NH_{org} + [Pd(NH_3)_2(H_2O)_2]^{2+}_{aq} + 3\,Salicylate^-_{aq} + H^+$$

4. Applications

4.1. Effect of diverse ions

In order to evaluate the suitability of the proposed method for extraction of palladium(II), the effect of some diverse ions was studied by adding different amounts of diverse ions to 200 µg of palladium(II) with 4-HAP (10 mL 0.05 M) in 0.04 M sodium salicylate. An error less than ±2% was considered to

Table 5
Effect of diverse ions on the extractive determination of palladium(II). Pd(II) = 200 µg, pH 0.5, Sodium salicylate = 0.04 M, 4-HAP = 0.05 M in xylene, contact time = 5 min, aq.: org. = 2.5:1

Amount tolerated (mg)	Diverse ion added
25	Te(IV)
15	Zn(II), Hg(II), chloride
10	Cu(II), Ni(II), Co(II), Cd(II), Bi(III), Sb(III), Mg(II), Sn(II), Pb(II)[b], Bromide, Citrate, Nitrate
5	Fluoride, Malonate, Acetate, Oxalate Cr(VI), Fe(III)[a], Fe(II)[a], Se(IV)[a], Ca(II)[c], In(III), Tl(I), U(VI)[a]
3	V(V)[a], Au(III)[e], Pt(IV)[d], Nitrate, Succinate
2	Tartarate, Ga(III)[d], Os(VIII)[f], Mo(II)[d], W(VI)[a], Ru(III)[f], Rh(III)[f]
1	EDTA, Sulphate, Iodide
0	Thiourea, thiosulphate, ascorbate

[a] Masked with 3 mg fluoride.
[b] Masked with 3 mg acetate.
[c] Masked with 7 mg citrate.
[d] Masked with 3 mg oxalate.
[e] Masked with 7 mg bromide.
[f] Masked with 12 mg chloride.

Table 6
Separation of palladium(II) from binary mixtures

Metal ion	Amount taken (μg)	Average recovery (%)[a]	Chromogenic ligand	Refs.
Pd(II)	200	99.8		
Fe(III)	60	98.5	Thiocyanate	[49]
Pd(II)	200	99.3		
Ni(II)	40	99.7	DMG	[49]
Pd(II)	200	99.3		
Co(II)	300	99.5	Thiocyanate	[49]
Pd(II)	200	99.5		
Cu(II)	40	99.4	2´, 4´-dinitro APTPT	[52]
Pd(II)	200	99.3		
Pt(IV)	300	99.6	Stannous chloride	[49]
Pd(II)	200	99.3		
Os(VIII)[b]	300	99.6	Thiourea	[50]
Pd(II)	200	99.9		
Ir(III)	80	99.7	Stannous chloride + hydrobromic acid	[49]
Pd(II)	200	99.9		
Ru(III)	200	99.7	Thiourea	[50]
Pd(II)	200	99.8		
Au(III)	200	98.9	Stannous chloride	[50]
Pd(II)	200	98.8		
Rh(III)	200	99.5	Potassium iodide	[49]
Pd(II)	200	99.8		
Hg(II)	100	98.4	PAN	[51]
Pd(II)	200	99.9		
Zn(II)	60	99.2	PAR	[51]
Pd(II)	200	99.9		
Pb(II)	100	99.0	PAR	[49]
Pd(II)	200	99.8		
Cd(II)	10	98.9	PAR	[51]
Pd(II)	200	99.9		
Bi(III)	300	99.0	Ascorbic acid + Potassium iodide	[49]
Pd(II)	200	99.7		
Te(IV)	40	99.1	4-Bromo PTPT	[54]
Pd(II)	200	99.9		
Ag(I)	150	98.9	2´,4´-dinitro APTPT	[53]

[a] Average of six determinations.

[b] Masked with 12 mg chloride.

be tolerable (Table 5). The selectivity of proposed method was enhanced by masking the tolerable cations with a suitable masking agent.

4.2. Separation of palladium(II) from binary mixtures

The separation of palladium(II) from the associated metal ions has been achieved under the optimum separation conditions in binary mixtures. At this condition, palladium(II) is extracted quantitatively leaving Fe(III), Ni(II), Co(II), Cu(II), Pt(IV), Os(VIII), Ir(III), Ru(III), Au(III), Rh(III), Hg(II), Zn(II), Pb(II), Cd(II), Bi(III), Te(IV), and Ag(I) in the aqueous phase from which they are determined spectrophotometrically by standard methods (Table 6). Palladium(II) from the organic phase was stripped and estimated spectrophotometrically by applying pyrimidine-2-thiol method.

4.3. Separation of palladium(II) from ternary mixtures

Palladium(II) selectively extracted from ternary mixtures. Palladium(II) is one of the PGMs, and therefore, palladium(II) was separated from Ag(I), Au(III); Ru(III), Rh(III); Ir(III), Pt(IV); Au(III), Pt(IV); and Os (VIII), Au(III). In this case, the Os(VIII) is masked by the suitable masking agent. All the PGMs are not extracted with 10 mL 4-HAP in xylene at 0.04 M sodium salicylate and pH 0.5. Palladium(II) was also

Table 7
Analysis of palladium(II) in synthetic mixtures corresponding to the composition of alloys

Alloy	Composition (%)	Palladium(II) taken (μg)	Palladium(II) Found (μg)	Relative recovery[a] (%)	RSD (%)
White gold	Au-75, Pd-10, Ni-10, Zn-5	10	9.9	99.1	0.84
Jewellery alloy	Pd-95.5, Ru-4.5	95.5	95.1	99.7	0.17
Pd–Cu	Pd-60, Cu-40	60	59.7	99.6	0.26
Stibio palladinite mineral	Pd-75, Sb-25	75	73.9	98.6	0.8
Oakay	(i) Pd-10.5, Pt-20, Ni-60, V-9.5	10.5	10.4	99.6	0.45
	(ii) Pd-18.2, Pt-18, Ni-54, V-9.5	18.2	18.0	98.9	0.71
Dental alloy	(i) Ag-45, Pd-50,Pt-2, Au-1	50	49.7	99.5	0.56
	(ii) Ag-15, Au-60, Pd-10, Pt-15	10	9.9	99.8	0.09
	(iii) Pd-34, Ni-34,Co-22, Au-10	34	33.8	99.4	0.37
Solder alloy	Pd-30, Pt-10, Au-60	30	29.8	99.4	0.52
Golden colour silver alloy	Pd-26, In-21, Cu-18, Ag-35	26	25.8	99.5	0.49
Pd–Au	Pd-50, Au-50	50	49.6	99.3	0.67
Autocatalyst	Pd-20, Pt-15, Rh-50	20	19.9	99.9	0.04

[a] Average of five determinations.

Table 8
Analysis of palladium(II) from different catalysts

Catalyst	Palladium added (μg)	Palladium found by proposed method (μg)	Relative recovery[a] (%)	RSD (%)
Pd on $BaSO_4$ (5%)	200	199.66	99.8	0.29
Pd on $BaCO_3$ (5%)	200	199.80	99.9	0.06
Pd on $CaCO_3$ (5%)	200	199.86	99.9	0.04
Pd on Carbon (10%)	200	199.40	99.7	0.33
Pd on Carbon (5%)	200	199.86	99.9	0.05

[a] Average of five determinations.

isolated from Cu(II), Co(II); Fe(III), Ag(I); Zn(II), Cu(II); Ni(II), Co(II); Fe(III), Cu(II); and Se(IV), Te(IV).

4.4. Analysis of palladium(II) from a Synthetic mixture corresponding to the composition of alloy

To ascertain the selectivity of the proposed method, it was successfully applied for the determination of palladium(II) in alloys from salicylate media at pH 0.5. The real samples were not available; hence the synthetic mixtures were prepared corresponding to the composition of the alloy. The results of the analysis are reported in (Table 7).

4.5. Analysis of palladium(II) in Catalyst

The proposed method is applicable for the determination of palladium(II) in various catalysts. A known amount of the catalyst was dissolved in a mixture of 9 and 3 mL of concentrated hydrochloric and nitric acid, respectively. The solution of catalyst is then heated with concentrated hydrochloric acid to remove the oxides of nitrogen. The residue was dissolved in 10 mL of 1.0 M hydrochloric acid and filtered to remove carbon or barium sulfate. The residue was washed with dilute HCl. The filtrate and washings were collected and diluted with water in a standard volumetric flask. An aliquot of the sample solution was taken, and palladium(II) was determined as per the general procedure. The results of the analysis are collected in (Table 8).

4.6. Determination of palladium(II) in different water samples

In order to investigate the accuracy and applicability of this method, real samples were analyzed. For the sample preparation, 200 μg of palladium(II) were spiked into the solutions and the results of recovery are shown in (Table 9).

Table 9
Determination of palladium(II) in different water samples

Sample	Palladium(II) spiked (μg)	Palladium(II) found (μg)	Relative recovery[a] (%)	RSD (%)
Distilled water	0.00	n.f.		–
	200	199.86	99.9	0.04
Tap water	0.00	n.f.		–
	200	199.80	99.9	0.06
Waste water	0.00	n.f.		–
	200	199.66	99.8	0.29
River water	0.00	n.f.		–
	200	199.40	99.7	0.33

[a] Average of five determinations.

Note: n.f. = not found.

5. Conclusion

The present investigations highlight that 4-HAP is a useful extractant for extraction of palladium(II) and also for their separation from most of the commonly associated metal ions. The separations can be accomplished at room temperature. The stripping agent used for separation is simple and convenient for further processing of solutions. In the earlier methods employed for extraction of palladium(II) the medium used was mineral acid, but in our proposed method we used a weak acid as a medium for extraction, in that sense our method is greener than the earlier. The developed conditions of extraction have been successfully extended to recover palladium(II) from synthetic mixture, alloys, catalysts, water samples, and binary and ternary metal ion mixtures. The method developed for the extraction of palladium(II) is very simple, selective, rapid, and cost effective for the separation and determination of palladium(II).

Acknowledgment

The authors are thankful to the University Grants Commission (UGC), New Delhi for research funding of the minor research project to the corresponding author. We are also thankful to the Department of Science and Technology (DST), New Delhi for providing funds to the Department of Chemistry, Shivaji University, Kolhapur under the FIST-Level-1 program for infrastructure improvement and UGC New Delhi for grants under the program UGC-DRS-I.

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