

## Spectrophotometric determination of palladium(II) with *N*-decylpyridine-4-amine from malonate media

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**Abstract :** Spectrophotometric determination of palladium(II) with *N*-decylpyridine-4-amine in xylene from malonate medium was carried out. Palladium(II) was extracted quantitatively with 10 ml of  $1 \times 10^{-4}$  M reagent concentration in xylene from 0.025 M sodium malonate concentration in 25 ml aqueous phase with 1 : 1 ammonia and estimated spectrophotometrically with pyridine-2-thiol at 410 nm. The effect of metal ions, acid, reagent concentrations and various foreign ions have been investigated. The method affords quantitative binary separation of palladium(II) and is applicable to the analysis of synthetic mixtures and alloys. The method is highly selective, simple and reproducible. The molar absorptivity and Sandell's sensitivity of palladium(II) *N*-decylpyridine-4-amine complex is ( $1.9 \times 10^5$  L mol<sup>-1</sup> cm<sup>-1</sup>) and (0.065 µg cm<sup>-2</sup>), respectively which indicates the applicability of the method.

**Keywords :** Palladium(II), *N*-decylpyridine-4-amine, solvent extraction, spectrophotometry.

### Introduction

The abundance of palladium in the earth's crust is  $8.5 \times 10^{-13}$  %. Palladium is a good catalyst and used in hydrogenation and dehydrogenation reactions<sup>1</sup>. Owing to its corrosion resistance properties and easy alloying, palladium and its alloys are also used in chemical industry, medical devices, pharmaceuticals, petroleum, electronics and in jewelry<sup>2</sup>. The increasing application of the platinum group metals in the industrial processes next to their extremely scarcity due to their natural abundance and the complexity of the process used for its extraction and refining, therefore, it is of paramount importance in the development of separation method to recover these metals to meet the future demand. Therefore, its separation and estimation at trace level is of significant importance<sup>3</sup>. Solvent extraction has become an effective technique in the recovery and separation of palladium<sup>4-7</sup>. Other extractants reported for palladium(II) are the methods reported are not so reliable for routine application because these suffer due to the drawbacks such as operating conditions (emulsion formation leading to problem for the separation, slow equilibrium) and ionic exchanger, nature of diluents, critical pH range etc. One co-ordination

chemistry property of palladium(II) is that it prefers to coordinate most strongly with polarisable atoms such as sulfur, phosphorus and nitrogen. 1,12-Di-2-thienyl-2,5,8,11-tetrathiaidodecane<sup>8</sup>, dithizone<sup>9</sup>, *N*-benzoyl *N,N'*-diethylthiourea<sup>10</sup>, hexadecylpyridiniumbromide (HDPB)<sup>11</sup>, 4-(2-pyridylazo)-resorcinol<sup>12</sup>, isoamylbenzothiazolyl sulfoxide<sup>13</sup>. These ligands are 'soft' bases according to the empirical Pearson's classification<sup>14</sup>. In last decade, various organic compounds such as 1-amino-4-hydroxy anthraquinone<sup>15</sup>, 5,6-dimethyl-1,3-indanedione-2-oxime<sup>16</sup>, 2-hydroxy acetophenone thiosemicarbazone<sup>17</sup>, isonitroso-4-methyl-2-pentanone<sup>18</sup>, 3,4,4a,5-tetrahydro-3,3,4a-trimethyl-7-(substituted)-pyrimido[1,6-*a*]benzimidazole thiol<sup>19</sup>, hexaacetaacalix[6]arene<sup>20</sup>, tetrabutylammonium-iodide<sup>21</sup> and 1,2-bis[methyl](2-aminocyclopentenecarbothioate)<sup>22</sup> have been reported as spectrophotometric reagents for the extraction and determination of palladium. However, the reported methods suffer from limitations such as interferences from other commonly associated ions<sup>23,24</sup>, negligible extraction and insufficient sensitivity<sup>25-27</sup>.

Nitrogen containing ligands are highly selective for extraction of palladium(II) and are highly water repellent.

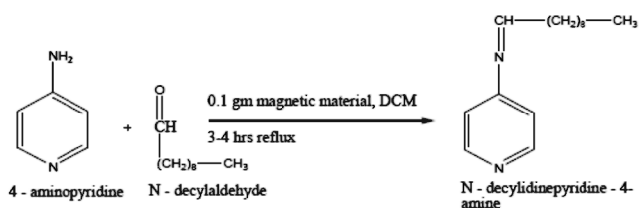
These does not form emulsion at the time of extraction. Aromatic and heteroaromatic amines are characterized by high extraction capacity and selectivity for platinum-group metals<sup>3</sup>. In the present investigation, *N*-decylpyridine-4-amine has been explored as a new reagent for the extraction and determination of palladium in microgram levels and has been considered as a most efficient technique for the recovery and separation of platinum-group metals (PGM) from organic acid media.

### Experimental

#### Synthesis of *N*-decylpyridine-4-amine :

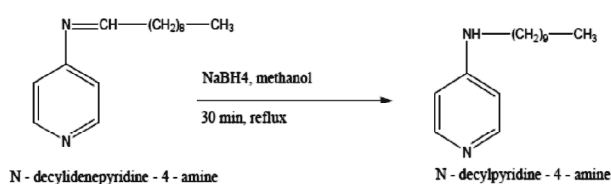
##### Step-1 :

*N*-Decylpyridine-4-amine was synthesized using equimolar proportion of *N*-decylaldehyde and 4-aminopyridine in 20 ml DCM and 0.1 mg of metal catalyst and was refluxed for 3–4 h. The product was separated and recrystallized from hot ethanol as white shiny needles (m.p. 68–70 °C).



##### Step-2 :

Product of step 1 (Schiff base) is reduced by NaBH<sub>4</sub> by taking equimolar amounts of Schiff base and NaBH<sub>4</sub> in absolute methanol and refluxed for 30 min, product was separated and recrystallized from hot ethanol (m.p. 245 °C).



The purity of compound was monitored using <sup>1</sup>H NMR, FT-IR and Mass spectra. <sup>1</sup>H NMR (CDCl<sub>3</sub>) : 0.87 (3H, t, -CH<sub>3</sub>), 1.87 (2H, d, -CH<sub>2</sub>), 1.26 (2H, d, -CH<sub>2</sub>), 3.4 (2H, s, -CH<sub>2</sub>), 4.1 (1H, s, -NH), 6.5 (2H, dd, *J* 8 Hz, aromatic protons), 8.2 (2H, d, *J* 8 Hz, aromatic protons); IR (cm<sup>-1</sup>) : 2922 (=C-H), 1331 (C-N), 1513–1640 (C=C), 3429 (N-H); Mass *m/e* : 236 (100.0%) ( M<sup>+</sup>).

#### Chemicals :

*N*-Decylpyridine-4-amine (1 × 10<sup>-4</sup> M) was used as an extractant; its solution was prepared in xylene. A stock solution of palladium(II) was prepared by dissolving 1 g of palladium chloride hydrate (S.D. Fine, India) in dilute analytical reagent grade hydrochloric acid (1 mol/dm<sup>3</sup>) and diluting to 100 ml with distilled water and further standardized gravimetrically<sup>23</sup>. A working solution 100 μg ml<sup>-1</sup> of Pd<sup>II</sup> was prepared from it by diluting the stock solution with distilled water. Other standard solutions of different metal ions used to study the effect of foreign ions were prepared by dissolving weighed quantities of respective salts in double distilled water or dilute hydrochloric acid. All the chemicals used were of A.R. grade. Double distilled water was invariably used throughout the measurements.

**Instruments :** A Jasco V-530 UV-Vis spectrophotometer with 1 cm quartz cell was used for absorbance measurements, pH measurements were carried out with Systronics digital pH Meter Model No. 802.

#### General procedure :

An aqueous solution containing 100 μg of palladium(II) mixed with sufficient quantity of sodium malonate (0.2 g) to make its concentration 0.025 M in total volume of 25 ml of the metal solution, then pH was adjusted in the range 7–10 using dilute hydrochloric acid and sodium hydroxide. The solution was transferred in to a 125 ml separating funnel and shaken with 10 ml *N*-decylpyridine-4-amine in xylene for 15–60 s. After equilibration, the mixture was allowed to separate and the metal was stripped from the organic phase with two 10 ml portions of 1 : 1 ammonia solution. The extract was evaporated to moist dryness. The residue was dissolved in 10 ml of pyrimidine-2-thiol solution and the absorbance of yellowish colored solution was measured at 410 nm against a reagent blank.

### Results and discussion

Palladium(II) reacts with extractant and forms 1 : 1 metal-ligand complex. The complex has maximum absorption at 410 nm. The molar absorptivity (1.9 × 10<sup>5</sup> L mol<sup>-1</sup> cm<sup>-1</sup>) and Sandell's sensitivity (0.065 μg cm<sup>-2</sup>), of the complex suggest that trace and ultra trace level quantities of palladium can be quantified with required accu-

racy and precision. The influence of various factors like pH, reagent concentration, choice of solvent and effect of foreign ions on the extraction efficiency of palladium(II) has been studied while optimizing the conditions for the selective and rapid extraction at trace level quantities.

*The spectral properties of the Pd-N-decylpyridine-4-amine :*

The absorption spectra of the Pd-*N*-decylpyridine-4-amine complexes were measured against a reagent blank, that of the reagent treated in a similar manner against a pyrimidine-2-thiol. The Pd-*N*-decylpyridine-4-amine complex has yellow colour and one strong absorbance peak at 410 nm. Therefore all the measurements have performed at 410 nm.

*Extraction as a function of pH :*

Palladium(II) was extracted in the pH range 7–10 in the presence of weak organic acids such as sodium salts of malonic acid (0.025 *M*) and succinic acid (0.001 *M*). Quantitative extraction of palladium(II) was observed in the pH range 7–10 from sodium malonate media and in the pH range 5–6 in salicylate media. There was incomplete extraction of palladium(II) from sodium succinate (75%) while no extraction was observed from sodium oxalate media (Fig. 1). Out of different organic acids

such as sodium salt of malonic acid, succinic acid, salicylic acid, tartaric acid, acetic acid, in tartaric acid, acetic acid and mineral acid media very less extraction was found. This shows that the equilibrium in the pH range 7–10 is favourable for the formation of ion pair complex from sodium malonate media. Hence sodium salt of malonate is used for further studies.

*Effect of N-decylpyridine-4-amine concentration :*

In order to optimize the conditions for the extraction of palladium(II), solutions of *N*-decylpyridine-4-amine with varying concentrations  $1 \times 10^{-5}$  –  $1 \times 10^{-1}$  *M* were employed at constant sodium malonate concentration. It was found that  $1 \times 10^{-5}$  *M* *N*-decylpyridine-4-amine was sufficient for quantitative extraction of 100  $\mu$ g palladium(II) from 0.025 *M* sodium malonate, but in recommended procedure  $1 \times 10^{-4}$  *M* concentration of *N*-decylpyridine-4-amine in xylene was used to ensure the complete extraction of metal ion. There was no adverse effect if one can use excess of extractant. However, a decrease in concentration of extractant resulted in lower distribution ratio, [D] for palladium(II).

*Effect of weak organic acid concentration :*

The study of the chlorocomplexes of the platinum group metals clearly indicates that the strength of interaction

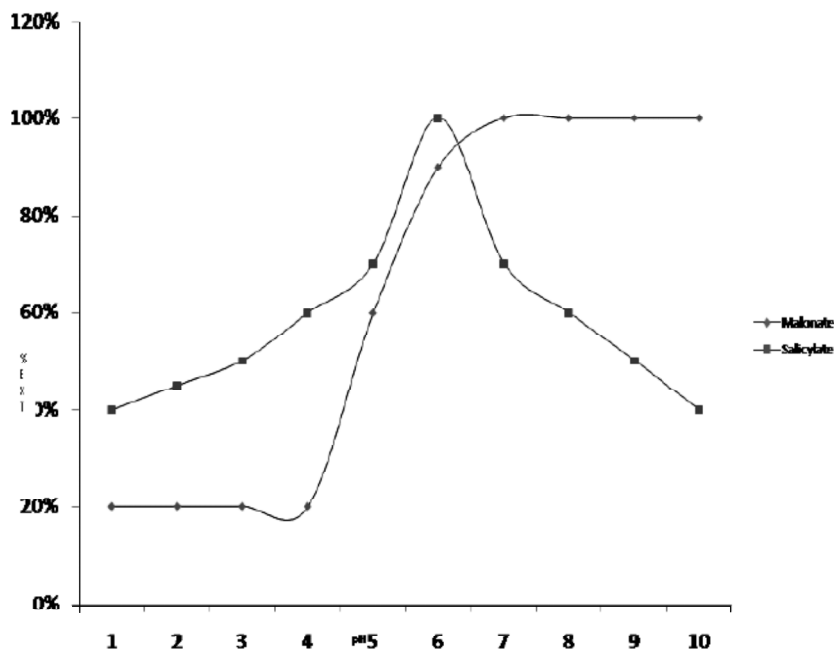


Fig. 1. Extraction of Pd<sup>II</sup> with  $1 \times 10^{-4}$  *M* *N*-decylpyridine-4-amine in xylene as a function of pH.

with ion exchangers is highly dependent on the charge of the complex. Therefore, the palladium(II) chlorocomplex is poorly extracted which is due to the charge of the complex as well as its labile in character towards aqution. Hence, it is worthwhile to develop the solvent extraction procedure in weak organic acid media. One of the distinct advantage of the malonate media is the facility of controlling the concentration of complexing ligand, the ease of adjustment of pH and wide differences in pH at which various metal ions form anionic complexes. It is observed that malonate media offers better phase separation possibly due to high stability of metal organic acid complex. The extraction of palladium(II) was carried out in pH range 7–10 with  $1 \times 10^{-4}$  M *N*-decylpyridine-4-amine in xylene in the presence of varying concentration of sodium malonate, sodium salicylate, sodium succinate and sodium oxalate as weak acid media and also in mineral acid media. The extraction of ion-pair complex of palladium(II) was found to be quantitative in the range of 0.02–0.03 M sodium malonate concentration. With increased concentration of sodium malonate there is decrease in the extraction of palladium(II). The decrease in the extraction at high acid concentration is presumably due to preferential formation of the malonate of the *N*-decylpyridine-4-amine. Therefore, a 0.025 M concentration of sodium malonate was used throughout this work. While extraction was found to be incomplete in mineral acid, and no extraction from sodium oxalate media.

*Effect of diluents :*

The extraction was performed from malonate medium using  $1 \times 10^{-4}$  M *N*-decylpyridine-4-amine in various solvents as diluents. It was found that ligand solution in carbontetrachloride, chloroform, toluene, benzene, xylene shows quantitative extraction of palladium(II). The extraction of palladium(II) was found to be incomplete in isobutylmethylketone, isoamylalcohol, *n*-butanol. Xylene is recommended for further extraction procedure as it is a nonpolar solvent. In nonpolar solvent in absence of repulsive forces, the extraction is maximum while in polar solvent the association of cationic species with extraction is minimum, xylene doesn't form emulsion and offers better phase separation.

*Effect of stripping agents :*

Stripping is the reverse of extraction, so it should be

promoted by those factors that affect extraction negatively, such as acidic and salt media. Stripping is removal of the extracted solute from the organic phase for further analysis. The conditions employed depends on the nature of metal ion and the particular extraction system and are such that they promote the reversal of extraction. The stripping of palladium(II) is quantitative with 1 : 1 ammonia solution. The stripping was found to be incomplete with nitric acid (60%), sulphuric acid (40%) and with sodium chloride (20%), where as palladium(II) was not stripped with, sodium hydroxide and water.

*Effect of aqueous to organic volume ratio :*

The results of contacting different volume ratios of organic to aqueous phase have been studied and a preferred aqueous/organic (A/O) phase ratio in this study was found to be 5 : 1 or less. This is evident from the sharp increase in the separation efficiency as well as the distribution ratio of palladium(II) when phase ratio (A/O) changed from 20 : 1 to 5 : 1. This may simply be due to the unavailability of reagent for metal extraction and so a crowding effect occurs at low phase ratio. However, in the recommended procedure the phase ratio is maintained as 2.5 : 1 so as to avoid the large consumption of sodium malonate.

*Effect of time on extraction :*

The effect of time was observed for a period of 5 s to 30 min (handshaking). The extraction was found quantitative over the periods longer than 10 s. But to ensure the complete extraction of palladium(II) 1 min time was recommended. However, a prolonged shaking period doesn't have any adverse effect on the extraction.

*Loading capacity of N-decylpyridine-4-amine :*

The loading capacity of the extractant was determined by the repeated contact of organic phase with a fresh feed solution of the metal of same concentration. For a 10 ml ( $1 \times 10^{-4}$  M) solution of *N*-decylpyridine-4-amine in xylene at 0.025 M sodium malonate concentration and a A/O of 2.5 : 1, the maximum loading capacity for palladium(II) was found to be 7.5 mg.

*Effect of various foreign ions :*

Palladium(II) was extracted in the presence of a large number of foreign cations and anions (Table 1). The tolerance limit was set out as the amount of the foreign ion

**Table 1.** Effect of foreign ions on the extraction of palladium(II)

Foreign ion	Added as	Tolerance limit (mg)	Foreign ion	Added as	Tolerance limit (mg)
Rh <sup>III</sup>	RhCl <sub>3</sub> .H <sub>2</sub> O	4	Sr <sup>II</sup>	Sr(NO <sub>3</sub> ) <sub>2</sub>	20
Pt <sup>IV</sup>	H <sub>2</sub> PtCl <sub>6</sub>	3	Pb <sup>II</sup>	Pb(NO <sub>3</sub> ) <sub>2</sub>	10
Au <sup>III</sup>	HAuCl <sub>4</sub>	4	Ti <sup>IV</sup>	K <sub>2</sub> .TiF <sub>6</sub> .H <sub>2</sub> O	15
Ru <sup>III</sup>	RuCl <sub>3</sub> .H <sub>2</sub> O	3	U <sup>VI</sup>	UO <sub>2</sub> (NO <sub>3</sub> ) <sub>2</sub> .6H <sub>2</sub> O	10
Cr <sup>III</sup>	CrCl <sub>3</sub>	10	Bi <sup>III</sup>	Bi(NO <sub>3</sub> ) <sub>3</sub> .5H <sub>2</sub> O	5
Mn <sup>II</sup>	MnCl <sub>2</sub> .6H <sub>2</sub> O	10	Iodide	Iodide	20
Co <sup>II</sup>	CoCl <sub>2</sub> .6H <sub>2</sub> O	30	Fluoride	Fluoride	25
Ni <sup>II</sup>	NiCl <sub>2</sub> .6H <sub>2</sub> O	25	Bromide	Bromide	20
Cu <sup>II</sup>	CuSO <sub>4</sub> .5H <sub>2</sub> O	30	Oxalate	Oxalate	25
Fe <sup>III</sup>	NH <sub>4</sub> Fe(SO <sub>4</sub> ) <sub>2</sub> .12H <sub>2</sub> O	20	Nitrate	Nitrate	20
Fe <sup>II</sup>	FeSO <sub>4</sub> .7H <sub>2</sub> O	20	Thiourea	Thiourea	20
Zn <sup>II</sup>	ZnSO <sub>4</sub> .7H <sub>2</sub> O	25	Succinate	Succinate	20
Hg <sup>II</sup>	HgCl <sub>2</sub>	20	Chloride	Chloride	25
Mg <sup>II</sup>	MgCl <sub>2</sub> .6H <sub>2</sub> O	30	EDTA	EDTA	50
Sn <sup>II</sup>	SnCl <sub>2</sub> .2H <sub>2</sub> O	15	Tartarate	Tartarate	50

that could be present to give an error less than  $\pm 2\%$  recovery of palladium(II). The reproducibility of palladium(II) extraction was investigated from six replicate measurements. After the phase separation, the organic phase was stripped with two 10 ml portions of 1 : 1 ammonia solution. The residue was dissolved in 10 ml of pyrimidine-2-thiol solution and palladium(II) was determined spectrophotometrically by pyrimidine-2-thiol <sup>24,25</sup>.

*Applications :*

*Binary separation of Pd<sup>II</sup> from Rh<sup>III</sup>, Pt<sup>IV</sup>, Au<sup>III</sup>, Ru<sup>III</sup>, Cu<sup>II</sup>, Co<sup>II</sup>, Ni<sup>II</sup>, Fe<sup>III</sup> :*

The method allowed separation and determination of Pd<sup>II</sup>, from a binary mixture containing Pd<sup>II</sup>, Rh<sup>III</sup>, Pt<sup>IV</sup>, Au<sup>III</sup>, Ru<sup>III</sup>, Cu<sup>II</sup>, Co<sup>II</sup>, Ni<sup>II</sup>, Fe<sup>III</sup>. In a typical experiment, solution containing 100  $\mu\text{g}$  of Pd<sup>II</sup> was taken and known amounts of other metals were added. Pd<sup>II</sup> was estimated spectrophotometrically. The recovery of Pd<sup>II</sup> and that of added ions was 99.5% and results are reported in Table 2.

*Analysis of synthetic mixtures :*

The separation of palladium(II) from other platinum group metals (platinum, rhodium, ruthenium and gold) and base metals was carried out by taking advantage of differences in their optimum extraction and stripping con-

**Table 2.** Separation and determination of palladium(II) from binary mixtures

Metal ion	Amount taken ( $\mu\text{g}$ )	Average (%) Recovery*	Ref.
Pd <sup>II</sup>	100	99.8	22
Rh <sup>II</sup>	100	99.7	
Pd <sup>II</sup>	100	99.9	22
Pt <sup>IV</sup>	300	99.8	
Pd <sup>II</sup>	100	99.8	22
Au <sup>II</sup>	300	99.8	
Pd <sup>II</sup>	100	99.9	22
Ru <sup>III</sup>	15000	99.9	
Pd <sup>II</sup>	100	99.8	23
Cu <sup>II</sup>	15000	99.9	
Pd <sup>II</sup>	100	99.9	23
Co <sup>II</sup>	10000	99.9	
Pd <sup>II</sup>	100	99.8	23
Ni <sup>II</sup>	10000	99.7	
Pd <sup>II</sup>	100	99.9	23
Fe <sup>III</sup>	10000	99.6	

ditions. The proposed method was successfully used in the determination of palladium(II) from different synthetic mixtures. A solution containing 100  $\mu\text{g}$  of palladium(II) was taken and known amounts of other metals were added. Under the optimum extraction conditions of palladium(II) there is quantitative extraction of Pd<sup>II</sup>, Pt<sup>IV</sup>, Ru<sup>III</sup> and

Au<sup>III</sup> but the co-extracted metal ions cannot be back stripped by 1 : 1 ammonia solution thus, the reagent *N*-

decylpyridine-4-amine is made selective towards palladium(II) by taking the advantage of stripping used.

*Analysis of alloys :*

The proposed method is applicable for the determination of palladium content in the thermocouple wire and alloy. Dissolution of sample is carried out by using literature method<sup>27,28</sup>. To ascertain the selectivity of the reagent, the proposed method was successfully used in the determination of palladium(II) in alloys. The synthetic mixtures were prepared corresponding to the composition of alloy. The results of the analysis are reported in Table 4. The average recovery of palladium(II) was 99.5%.

**Conclusion**

In the present work, a simple, sensitive, inexpensive and selective method was developed for the extraction and separation of palladium(II) from binary mixtures, synthetic mixtures and alloys. The proposed method has several remarkable analytical characteristics :

- (i) It is free from interference from the large number of diverse ions which are associated with palladium(II) in its natural occurrence.
- (ii) The important features of this method are that low reagent concentration is required, and the time required for the equilibrium is very short (30 s).
- (iii) The method is very simple, selective and reproducible.

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**Table 3.** Analysis of synthetic mixture

Composition (µg)	Palladium(II) found (µg)	Mean	Recovery (%)	RSD (%)
Pd, 100; Pt <sup>b</sup> , 500; Ru, 200	199.7	199.74	99.94	0.07
	199.7			
	199.8			
	199.7			
	199.8			
Pd, 100; Pt <sup>b</sup> , 500; Rh <sup>a</sup> , 500	199.9	199.86	99.92	0.09
	199.8			
	199.9			
	199.9			
	199.8			
Pd, 500; Au, 100; Pt <sup>b</sup> , 200	199.8	199.84	99.94	0.07
	199.8			
	199.8			
	199.9			
	199.9			
Pd, 100; Pt <sup>b</sup> , 500; Ru, 500; Au, 500	199.9	199.86	99.96	0.05
	199.8			
	199.9			
	199.8			
	199.9			
Pd, 100; Pt <sup>b</sup> , 500; Rh <sup>a</sup> , 500; Au, 500	199.8	199.76	99.98	0.06
	199.7			
	199.8			
	199.8			
	199.7			
Pd, 100; Fe, 1000; Cu, 1000; Ni, 500	199.9	199.86	99.96	0.05
	199.9			
	199.9			
	199.8			
	199.8			

<sup>a</sup>Masked with tartarate. <sup>b</sup>Masked with oxalate.

**Table 4.** Analysis of synthetic mixtures corresponding to alloy

Alloys	Composition (%)	Amount of palladium(II) found by proposed method <sup>a</sup> (%)	RSD <sup>b</sup> (%)
Palladium-Rhodium thermocouple wire	Pt, 87; Rh 13	86.8	0.45
Palladium-Rhodium alloy	Pd, 90; Rh 10	89.4	0.46

<sup>a</sup>Average of five determinations.

<sup>b</sup>RSD (%) = (Standard amount – amount found/standard amount) × 100.

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