

## SIMULTANEOUS COPRECIPITATION OF Pd(II), Rh(III) AND Au(III) WITH Mn(OH)<sub>2</sub> WITHOUT CHELATING AGENT PRIOR TO FLAME ATOMIC ABSORPTION SPECTROMETRY DETERMINATION

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### ABSTRACT

A separation-preconcentration procedure was developed for determination of trace amounts of palladium, rhodium and gold in dust and water samples by flame atomic absorption spectrometry after simultaneous coprecipitation by Mn(OH)<sub>2</sub> without chelating agent. The precipitate could be easily dissolved with concentrated nitric acid. The influence of the various analytical parameters such as pH, sample volume, centrifuge time, standing time, centrifugation rate and time, amounts of manganese and matrix effects were studied for the quantitative recoveries of the analyte ions. Under the optimized experimental conditions, the calibration curves for Pd(II), Rh(III) and Au(III) were linear from 8.0 to 2000.0, 1.0 to 750.0 and 5.0 to 1000.0 ng mL<sup>-1</sup>, respectively. The relative standard deviations for seven replicate determinations of a mixture of 0.1 µg mL<sup>-1</sup> palladium, rhodium and gold in the original solution were 2.1, 1.9 and 2.4%, respectively. The detection limits based on 3S<sub>n</sub> for Pd(II), Rh(III) and Au(III) in the original solution were 2.2, 0.3 and 1.3 ng mL<sup>-1</sup>, respectively. The proposed method has been applied for determination of trace amounts of palladium, rhodium and gold ions in the standard, road dust and water samples and satisfactory results were obtained.

**Keywords:** Palladium; Rhodium; Gold; Coprecipitation; Preconcentration; FAAS; Road dust and water samples

### INTRODUCTION

Heavy metals at trace levels are considerably toxic even in very low concentration of environmental pollution. The importance of heavy metals pollution control has increased significantly in the recent decades.<sup>1</sup> Trace element contamination presents a significant threat to the ecosystem due to severe toxicological effects on living organisms.<sup>2-6</sup>

The determination of trace heavy metals ions in environmental samples by flame atomic absorption spectrometry (FAAS) is directly difficult even with background correction and chemical modification; not only because of the presence of many trace metals at concentrations near or below detection limit, but also because of sample matrix may cause serious interference.<sup>7-11</sup> In order to solve these problems, separation-enrichment techniques including solid phase extraction, cloud point extraction, liquid-liquid extraction, coprecipitation, etc.<sup>12-18</sup> have been used by the researchers around the world.

Coprecipitation has also an important place in the preconcentration and separation methods due to its some advantages including simplicity, high preconcentration factors, and low consumption of organic solvent and short analysis time period for the procedures.<sup>19-23</sup> In the coprecipitation procedure, a precipitate was occurred by the combination of a carrier element and a suitable inorganic or organic ligand. Various carrier elements including copper, nickel, aluminum, erbium, magnesium, indium, samarium, etc. have been used for the preconcentration and separation of heavy metal ions at traces levels.<sup>24-29</sup> Inorganic ligands like hydroxide, thiocyanate and organic ligands like various ditiocarbamates, 5-methyl-4-(2-thiazolylazo) resorcinol, rubeanic acid, etc. have been used for this purpose.<sup>24-28</sup>

According to our literature survey, Mn(II) is not used for the coprecipitation without chelating agent, until now. In this study, a separation/preconcentration procedure using coprecipitation for palladium, rhodium and gold ions has been developed prior to FAAS determination. The analytical parameters were investigated and optimized.

### EXPERIMENTAL

#### Instrumentation

A SensAA GBC atomic absorption spectrometer (Dandenong, Australia) equipped with deuterium background correction and air-acetylene burner was used for absorbance measurements. Palladium, rhodium and gold hollow cathode lamps were used as light source at wavelengths of 244.8, 343.5 and 242.8 nm, respectively. The operating parameters of elements were set according to the manufacturer recommendation. 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. A Centurion scientific centrifuge model 1020 D.E. (West Sussex, United Kingdom) was used to

accelerate the phase separation.

#### Reagents and Solutions

Deionized water was used throughout the experimental work. The stock solution of rhodium was prepared from Rh(III) standard solution 1000.0 mgL<sup>-1</sup> (Merck, Darmstadt, Germany) by serial dilution with deionized water. The stock solutions of palladium and gold at a concentration of 1000.0 µg mL<sup>-1</sup> were prepared by dissolving appropriate amounts of PdCl<sub>2</sub> and HAuCl<sub>4</sub>·xH<sub>2</sub>O (Merck) in 2.0 mol L<sup>-1</sup> HCl. Working standard solutions were obtained by appropriate dilution of the stock standard solution by serial dilution with deionized water. The laboratory glassware was kept overnight in a 1.4 mol L<sup>-1</sup> HNO<sub>3</sub> solution. Before using, all of the glassware were washed with de-ionized water and dried. 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. Diluted HNO<sub>3</sub> and NaOH solution were used for pH adjustments.

#### Coprecipitation procedure

The coprecipitation procedure was optimized with aqueous solutions prior to its application to the real samples. First, 30.0 mL portions of an aqueous solution containing 0.1 µg of Pd(II), Rh(III) and Au(III) were given and pH of solution was adjusted to 10.0. Then, 2.0 mL of 1000.0 mg L<sup>-1</sup> of Mn(II) as a carrier element was poured into the tube. After 10 min, the solution was centrifuged at 4000 rpm for 6 min. The supernatant was removed. The precipitate remained adhering to the tube was dissolved with 2.0 mL of concentrated HNO<sub>3</sub>. The final solution was aspirated directly into the flame of FAAS.

#### Sample preparation for standard and real samples

One platinum-iridium alloy was analyzed. To 5.0 mg of this alloy, 7 mL of aqua regia was added and the solution was heated. After this, 5 mL of concentrated hydrochloric acid was added to it and was warmed. Then, the solution was cooled and made to 1000.0 mL with deionized water in a calibrated flask.

The road dust samples were collected from three different roadsides having dense traffic in Kerman in Iran. The samples were dried at 100 °C for 2 h, ground, passed through a sieve of 200 meshes and the homogenized. 10.0 g of each sample was weighed into a 100 mL of beaker. In order to decompose it, 20 mL of aqua regia was added to the beaker and the mixture was heated almost to dryness. Then, 15 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 deionized water. The pH was adjusted to 8 and the total volume was made up to 100.0 mL with deionized water in calibrated flasks.

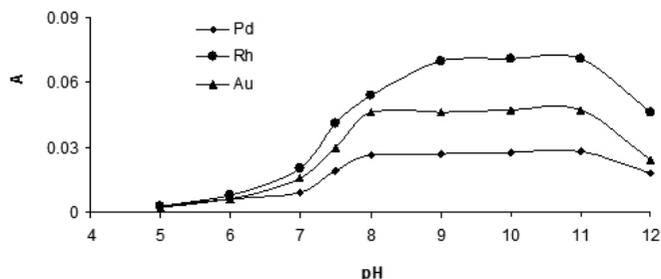
River water and wastewater samples were collected in acid leached polyethylene bottles. Before the analysis, the organic content of the water samples was oxidized in the presence of 1% H<sub>2</sub>O<sub>2</sub> and then was acidification

to pH 2 with nitric acid. River water sample was collected from Kohpayeh (Kerman, Iran) and wastewater samples were collected from copper factory in Sarcheshmeh area (Kerman, Iran) and Bahonar copper factory in Kerman. The samples were filtered before analyses through a cellulose membrane (Millipore, Bedford, MA, USA).

## RESULTS

### Effects of pH

The influence of the pH on the recovery of trace level of Pd(II), Rh(III) and Au(III) were examined. Manganese hydroxide could be obtained at pHs higher than 6.0. The pH was adjusted to 5–12 by changing the amount of added NaOH solution while the amount of manganese in solution was constant. As can be seen from Fig. 1, the absorbance of all elements increased with increase of pH and maximum absorbances were obtained for all studied elements at pH range 9–11. For further experiments, pH 10 was chosen as optimum pH.

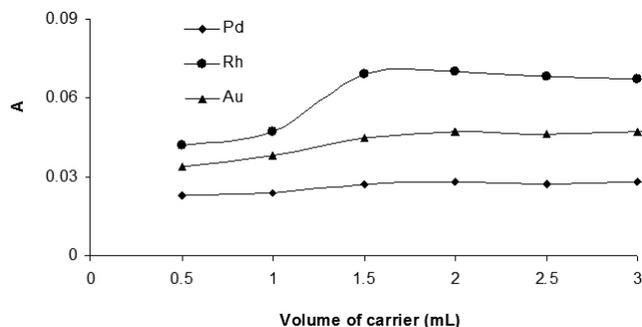


**Fig. 1.** Effect of pH on the coprecipitation procedure of Pd(II), Rh(III) and Au(III) ions

Conditions: Pd(II), Rh(III) and Au(III), 0.1  $\mu\text{g}$ ; Mn(II), 2.0 mL of 1000  $\text{mg L}^{-1}$ ; Standing time, 10 min; Centrifugation time, 6 min at 4000 rpm.

### Effects of amount of Mn(II) as carrier element

The influence of amount of Mn(II) as carrier element on the recovery of palladium, rhodium and gold ions were also investigated. The results are shown in Fig. 2. As can be seen from Fig. 2, the absorbance of all elements increased with increase of amount of carrier element and maximum absorbances were obtained for all studied elements at the range of 1.5–3.0 mg. In the light of these results, 2.0 mg of Mn(II) was used in all further works.



**Fig. 2.** The influence of amount of carrier element on the coprecipitation procedure of Pd(II), Rh(III) and Au(III) ions

Conditions were the same as Fig. 1 except to volume of Mn<sup>2+</sup>

### Effect of standing time

For investigation of standing time of solution on the recovery of palladium, rhodium and gold ions, 2.0 mL of Mn(II) were added into a series of solutions, containing 0.1  $\mu\text{g}$  of Pd(II), Rh(III) and Au(III). Then, standing time was investigated in the range of 0–15 min. The results were showed that after 7 min, quantitative recoveries were obtained. Therefore, 10 min was selected as optimum standing time for all subsequent experiments.

### Effect of centrifugation time

The influence of centrifugation time on the recoveries of Pd(II), Rh(III) and Au(III) ions were also investigated in the range of 2–15 min at 4000 rpm. The results were showed that, quantitative recoveries were obtained for analyte

ions in the range of 5–15 min. Therefore, 6 min was selected as optimum centrifugation time at 4000 rpm.

### Effect of sample volume

The volume of aqueous solution is a critical and important factor in the coprecipitation of the metal ions to obtain high preconcentration factors. In order to, a series of sample solutions, containing 2  $\mu\text{g}$  of palladium, rhodium and gold ions were prepared in the volume range 20 to 300 mL and recoveries of the analyte ions measured at the optimum conditions. The results showed that Pd(II), Rh(III) and Au(III) ions were quantitatively recovered when the sample volume was less than 250 mL. When the sample volume exceeded 250 mL, the recovery of the analyte ions decreased. Consequently, by considering the final elution volume (2.0 mL) and a breakthrough volume of 250 mL, a preconcentration factor of 125 was easily achievable.

### Effect of foreign ions

The influence of matrix ions were also investigated. For this purpose, a fixed amount of Pd(II), Rh(III) and Au(III) ions were taken with different amounts of foreign ions and recommended procedure was followed. Tolerable limit was defined as the highest amount of foreign ions that produced an error not exceeding  $\pm 5\%$  in the determination of the analyte ions. The results are shown in Table 1. The results showed that large number of anions and cations used have no considerable effect on the determination of the analyte ions. Also some transition metals at  $\text{mg L}^{-1}$  levels were not interfered on the recoveries of the analyte ions. As a result, the coprecipitation procedure could be applied to the highly saline samples and the samples that contain some transition metals at tolerable level given in Table 1.

**Table 1** Tolerance limit of foreign ions.

Foreign ions	Interference/Analyte ions ratio		
	Pd(II)	Rh(III)	Au(III)
$\text{H}_2\text{PO}_4^-$ , $\text{HPO}_4^{2-}$	4000	5000	5000
$\text{Ca}^{2+}$	1500	2000	2000
$\text{Mg}^{2+}$	2000	2500	2000
$\text{Al}^{3+}$	500	500	350
$\text{Ag}^+$	500	500	500
$\text{Cu}^{2+}$	500	500	300
$\text{Cr}^{3+}$	500	500	250
$\text{Zn}^{2+}$	500	400	250
$\text{Fe}^{2+}$	500	500	500
$\text{Co}^{2+}$	500	250	400
$\text{Cd}^{2+}$	500	500	350
$\text{Ni}^{2+}$	500	250	500
$\text{Pb}^{2+}$	500	500	300

Conditions were the same as Fig. 1.

### Figure of merits

Under the optimized conditions, calibration curves were constructed by coprecipitation 50.0 mL of a sample solution containing of known amounts of the analyte ions. Linearity was maintained between 8.0  $\text{ng mL}^{-1}$  to 2.0  $\text{mg mL}^{-1}$  for Pd(II), 1.0  $\text{ng mL}^{-1}$  to 0.75  $\text{mg mL}^{-1}$  for Rh(III) and 5.0  $\text{ng mL}^{-1}$  to 1.0  $\text{mg mL}^{-1}$  for Au(III). Seven replicate determination of a mixture of 0.1  $\mu\text{g mL}^{-1}$  palladium, rhodium and gold in the original solution gave a mean absorbance of 0.071, 0.113 and 0.089 with relative standard deviation 2.1%, 1.9% and 2.4%, respectively. The detection limits based on  $3S_0$  for Pd(II), Rh(III) and Au(III) in the original solution were 2.2, 0.3 and 1.3  $\text{ng mL}^{-1}$ , respectively. The analytical parameters are given in Table 2.

**Table 2** Analytical parameters of the method

Statistical parameters	Palladium	Rhodium	Gold
Linear ranges ( $\text{ng mL}^{-1}$ )	8.0-2000.0	1.0-750.0	5.0-1000.0
Regression equations	$A=0.483X+0.0012$	$A=1.1887X+0.0029$	$A=0.8049X+0.0034$
Correlation coefficient (R)	0.9993	0.9999	0.9995
RSD%	2.1	1.9	2.4
Detection limit ( $\text{ng mL}^{-1}$ )	2.2	0.3	1.3

*Validation of the method*

The coprecipitation procedure was evaluated using one platinum-iridium alloy. The results are given in Table 3. The obtained results were in good agreement with the certified values. These results indicate the accuracy of the coprecipitation procedure for preconcentration of the analyte ions.

**Table 3** Determination of the analyte ions in platinum-iridium alloy.

Composition (%)	Certified value (%)	Found value <sup>a</sup> (%)
Pt, 55; Ir, 28; Cu, 3.0; Fe, 3.5	Pd: 3.5 Rh: 7.0 Au: 2% was added	3.57±0.12 6.95±0.24 2.04±0.07

<sup>a</sup> Average of three determinations±standard deviation

*Applications*

The coprecipitation procedure has been applied to the determination of palladium, rhodium and gold content in different water samples. The results are given in Table 4. Also, the coprecipitation procedure has been applied for preconcentration of the analyte ions in road dust samples. The results are given in Table 5.

The recovery of palladium, rhodium and gold from water and road dust samples spiked with Pd(II), Rh(III) and Au(III) ions were also studied. The results are given in Tables 4 and 5. According to this results, the added Pd(II), Rh(III) and Au(III) ions can be quantitatively recovered from the water and road dust samples by the coprecipitation procedure. These results demonstrate the applicability of the procedure for palladium, rhodium and gold determination in water and road dust samples.

**Table 4** Determination of Pd(II), Rh(III) and Au(III) in water samples.

Sample	Found <sup>a</sup> (ng mL <sup>-1</sup> )	Added (ng mL <sup>-1</sup> )	Found (ng mL <sup>-1</sup> )	Recovery (%)
River Water (Kohpayeh, Kerman)	Pd: ND <sup>b</sup> Rh: ND Au: ND	Pd: 5.0 Rh: 5.0 Au: 5.0	Pd: 5.14±0.21 Rh: 4.93±0.24 Au: 5.07±0.26	102.8 98.6 101.4
Wastewater (Copper factory, Sarchashmeh, Rafsanjan)	Pd: ND Rh: ND Au: 6.5±0.05	Pd: 5.0 Rh: 5.0 Au: 5.0	Pd: 4.97±0.25 Rh: 5.17±0.20 Au: 11.41±0.05	99.4 103.4 98.2
Wastewater (Copper factory, Shahid Bahonar, Kerman)	Pd: ND Rh: ND Au: 5.9±0.05	Pd: 5.0 Rh: 5.0 Au: 5.0	Pd: 4.88±0.21 Rh: 4.94±0.06 Au: 11.07±0.05	97.6 98.8 103.4

<sup>a</sup> Average of three determinations±standard deviation

<sup>b</sup> ND: Not Detect

**Table 5** Determination of the analyte ions in the road dust samples.

Sample	Found (µg g <sup>-1</sup> ) <sup>a</sup>	Found (µg g <sup>-1</sup> ) <sup>b</sup>	Recovery (%)
Street dust No. 1	Pd: 0.23±0.01 Rh: 0.33±0.02 Au: ND <sup>c</sup>	Pd: 1.24±0.05 Rh: 1.37±0.06 Au: 0.98±0.05	101.0 104.0 98.0
Street dust No. 2	Pd: 0.21±0.01 Rh: 0.38±0.02 Au: ND	Pd: 1.18±0.04 Rh: 1.40±0.05 Au: 1.01±0.04	97.0 102.0 101.0
Street dust No. 3	Pd: 0.26±0.02 Rh: 0.40±0.02 Au: ND	Pd: 1.30±0.05 Rh: 1.38±0.05 Au: 0.97±0.04	104.0 98.0 97.0

<sup>a</sup> Average of three determinations±standard deviation

<sup>b</sup> 1.0 µg g<sup>-1</sup> of the analyte ions were added and then measured.

<sup>c</sup> ND: Not Detect

**CONCLUSIONS**

The coprecipitation with manganese hydroxide system without chelating agent is firstly used in the present work for preconcentration of the analyte ions in various water samples, road dust and certified samples. The main benefits of the coprecipitation procedure were: simplicity, low cost, enhancement of sensitivity, rapid analysis time and high enrichment factor. Also, the coprecipitation procedure does not need any chelating agent.

A comparison of the present method with the other reported preconcentration methods<sup>29-33</sup> for the gold, palladium and rhodium extraction was given in Table 6. As can be seen, the presented coprecipitation method for the separation and preconcentration of Pd(II), Rh(III) and Au(III) ions, exhibits a high preconcentration factor and low LOD in most cases than the previously reported methods.

**Table 6** Comparison of the coprecipitation procedure with other reported methods for preconcentration of the analyte ions.

System	Analysis method	P.F. <sup>a</sup>	RSD (%)	Linear range (ng mL <sup>-1</sup> )	LOD (ng mL <sup>-1</sup> )	Ref.
Coprecipitation	FAAS	25	< 10	-----	Pd: 1.5 Au: 2.1	29
Solid phase extraction	FAAS	----	Pd: 1.7 Au: 1.2	Pd: 200-4000 Au: 200-3000	Pd: 17 Au: 13	30
Coprecipitation	FAAS	100	6.3	-----	Pd: 0.4	31
Dispersive liquid-liquid micro-extraction	FAAS	45.7 <sup>a</sup>	0.7	-----	Pd: 90	32
Cloud point extraction	FAAS	30	2.7	-----	Pd: 8.9	33
Coprecipitation	FAAS	125	Pd: 2.1 Rh: 1.9 Au: 2.4	Pd: 8.0-2000.0 Rh: 1.0-750.0 Au: 5.0-1000.0	Pd: 2.2 Rh: 0.3 Au: 1.3	Present work

<sup>a</sup> Preconcentration factor

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