

## 펄스 차이 폴라로그래피법에 의한 미량 백금과 로듐의 동시 정량

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## Simultaneous Determination of Traces of Platinum and Rhodium by Differential Pulse Polarography

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**요 약.** 백금과 로듐 모두 미량으로 존재할 때 펄스 차이 폴라로그래피법으로 동시 정량할 수 있는 용액조건을 확립하였다. 포름알데히드 0.004%(w/v)-히드라진 0.0012%(w/v)-황산 0.75 M의 조건에서 가장 예민한 수소 촉매파를 얻을 수 있었다. 이 조건에서 단일 금속의 검출 한계는  $7.3 \times 10^{-11}$  M Pt 그리고  $3.2 \times 10^{-11}$  M Rh이었다. 봉우리 전류가 선형인 농도범위는 백금이  $5 \times 10^{-10} \sim 6 \times 10^{-8}$  M이고 로듐은  $1 \times 10^{-10} \sim 2 \times 10^{-8}$  M이었다. 이 농도범위에서 로듐(10배 이상)과 이리듐(100배 이상)만이 백금을 방해하였다. 로듐은 어떠한 여타 백금족 원소(1000배 이상의 백금, 500배의 이리듐 존재하에서도)의 방해도 받지 않았다.

**ABSTRACT.** Simultaneous measurements of trace platinum and rhodium, based on catalytic reduction of protons by the adsorbed Pt-formazone and Rh-formaldehyde complexes formed in formaldehyde-hydrazine-sulfuric acid medium, were demonstrated. The conditions for the measurements of Pt and Rh both present at trace levels ( $>10^{-10}$  M) were 0.004% (w/v) formaldehyde-0.0012% (w/v) hydrazine-0.75 M sulfuric acid. In this medium method detection limits are  $7.3 \times 10^{-11}$  M Pt and  $3.2 \times 10^{-11}$  M Rh. And dynamic ranges are  $5 \times 10^{-10} \sim 6 \times 10^{-8}$  M and  $1 \times 10^{-10} \sim 2 \times 10^{-8}$  M for platinum and rhodium respectively. In the linear dynamic ranges, Rh and Ir interfere platinum in the presence of only 10 and 100 times that of Pt respectively. There are no interferences from other platinum group metal ions for rhodium even in the presence of a 500-fold excess of Ir(IV), a hundredfold excess of platinum.

### INTRODUCTION

Determination of precious platinum group metals (PGMs), especially at trace and ultratrace levels, is becoming increasingly important in various area of modern technologies. PGMs are readily determined by polarographic methods. Small

amounts of PGM ions ( $<10^{-6}$  M) can be determined from the catalytic hydrogen currents arising on the dropping mercury electrode in an acidic medium containing suitable complexing ligands<sup>1</sup>. Most of the recent studies have been devoted to development of selective scheme for a single ion

since most PGMs display catalytic hydrogen waves and interfere with each other. Various supporting electrolyte media (acids), different complexing ligands, and corresponding detection limits or linear dynamic ranges were reviewed by Zhao and Freiser<sup>2</sup> for the determination of trace platinum. They also suggested that rhodium(III) gives a catalytic waves at  $-1.16$  V vs. Ag/AgCl, just following the catalytic wave of platinum (at  $-1.0$  V) in 0.02% (w/v) formaldehyde-0.002% (w/v) hydrazine-0.75 M H<sub>2</sub>SO<sub>4</sub> medium. Hence, the method may be used for the simultaneous determination of platinum and rhodium.

In this paper, detailed information about the simultaneous measurement capability for platinum and rhodium in formazone-sulfuric acid medium is given. During the last two decades, a substantial improvement in detectability has been achieved for platinum. The detection limit of ca.  $10^{-8}$  M in 1970s<sup>3</sup> has lowered to  $10^{-11}$  M in 1992<sup>4</sup> by coupling the catalytic current with adsorption of the catalyzer and with differential pulse measurements. In contrast, there are only a few catalytic hydrogen schemes for the determination of rhodium<sup>5,6</sup>.

In the course of the present work, the complexing properties of the formaldehyde-hydrazine media with respect to both platinum and rhodium were exploited to determine simultaneously both metals present at the subnanomolar level. The present results indicate that the formation of surface active complexes, platinum-formazone<sup>2</sup> and rhodium-formaldehyde(likely the bonding mode is side-on ( $\eta^2$ -C, O) with metal cluster<sup>7</sup>), when coupled with hydrogen catalytic process, constitutes the bases for an ultrasensitive differential pulse polarographic (DPP) method for multielemental determination, with a remarkably low detection limit of  $7.3 \times 10^{-11}$  M Pt and  $3.2 \times 10^{-11}$  M Rh. Furthermore, rhodium complex is very stable and specific, hence rhodium measurement is not interfered with other PGMs, even by a 500-fold excess of Ir(IV). A powerful analytical scheme thus results from the coupling of excellent sensitivity, low cost, simple, and multielement capability.

## EXPERIMENTAL

**Apparatus and reagents.** A PAR 264 voltammetric analyzer with a PAR303A static mercury drop electrode (smde) and an X-Y recorder (PAR Model RE0089) were used for the polarographic measurements. For differential pulse polarographic (DPP) operation, the parameters were as follows: 0.5-s drop time, 5 mV/s scan rate, and 25-mV modulation amplitude. A medium-size dropping mercury electrode (0.017-cm<sup>2</sup> surface area) was used as the working electrode. All solutions of PGMs were atomic absorption standard solutions purchased from Aldrich Chemical Co. Inc., and Junsei Co. All other solutions were prepared from analytical-reagent grade chemicals. Solutions of formaldehyde and hydrazine were prepared separately and were mixed freshly daily. It was not necessary to remove oxygen from the solution as it does not affect the polarographic wave at all. All data were obtained at room temperature ( $22 \pm 2$  °C).

**Procedure.** A 10-mL volume of the supporting electrolyte solution containing 0.004% (w/v) formaldehyde, 0.0012% (w/v) hydrazine, 0.75 M sulfuric acid, and various amounts ( $10^{-7}$ ~ $10^{-10}$  M) of platinum and rhodium, was introduced into the cell. The DP polarograms (dpp) were recorded from  $-0.7$  to  $-1.35$  V (vs. Ag/AgCl). Peak currents ( $I_p$ ) of the dpp were measured in usual way.

## RESULTS AND DISCUSSION

**Catalytic waves caused by rhodium complexes.** Some dpp recorded in 0.02% (w/v) formaldehyde-0.002% (w/v) hydrazine-0.75 M sulfuric acid medium are shown in Fig. 1. It appears from the solution conditions for the dpps in Fig. 1 that a broad peak (A on Curve 2) around  $-0.95$  V and large peak B, at  $-1.2$  V, are due to the reduction of formazone<sup>2</sup> and formaldehyde<sup>8</sup> respectively. A catalytic wave caused by a rhodium complex (C on curve 3, at ca.  $-1.32$  V) is ill-defined and interfered with by overlapped formaldehyde peak B. As expected, the problem of overlapping peaks can be overcome by decreasing the formaldehyde concentration. Typical dpps recorded in 0.004% (w/v)

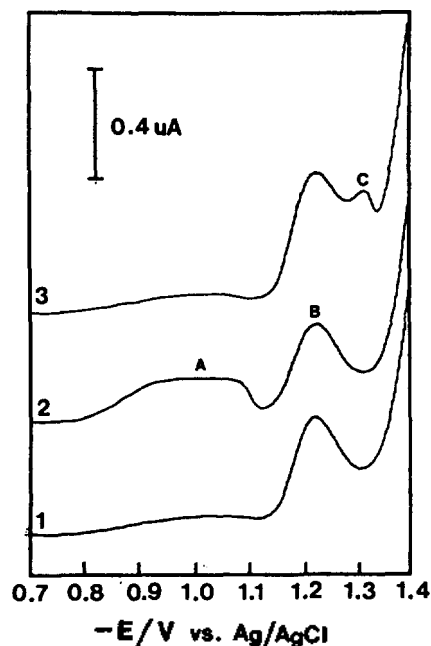


Fig. 1. DP polarograms of solutions containing 0.75 M  $H_2SO_4$ -0.02% (w/v) formaldehyde (1); (1)+0.002% (w/v) hydrazine (2); (1)+ $1.94 \times 10^{-10}$  M Rh (3).

formaldehyde - 0.0012% (w/v) hydrazine - 0.75 M sulfuric acid medium are shown in Fig. 2. Unlike platinum which gives only one wave (A on curve 3), rhodium gives rise to two catalytic hydrogen waves (peaks B and C on curve 2) in the medium. Because of the low sensitivity (appears only in the concentration of rhodium higher than  $1.0 \times 10^{-8}$  M), peak B (suggested by previous workers<sup>2</sup> as a potential analytical peak for rhodium measurement) is not feasible as an analytical wave for trace determination of rhodium simultaneously with platinum. The low sensitivity is attributed to the lability and instability of the rhodium-formazone complex compared to platinum-formzone and to a rhodium-formaldehyde complexes. Large and stable peak (C on curve 2) occurring at -1.28 V (peak potential is shifted toward negative upon increasing the formaldehyde concentration -1.5 V/%- in formazone media) in the presence of formaldehyde alone, instead, is the most suitable were for the measurement of trace rhodium in the presence of PGMs. The complex species for which is the C peak responsible is not clear and

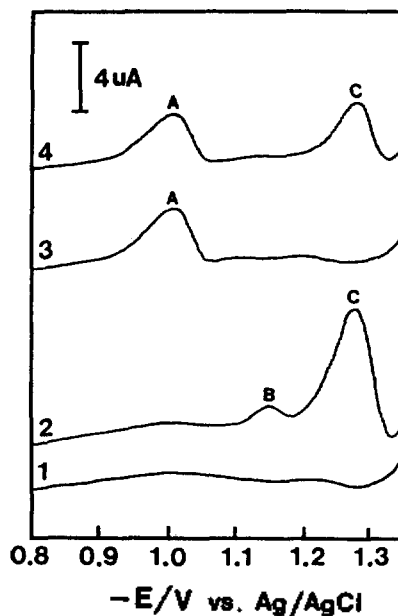


Fig. 2. Typical dpps in 0.004% (w/v) formaldehyde-0.0012% (w/v) hydrazine-0.75 M  $H_2SO_4$  medium for: (1) blank; (2)  $1.94 \times 10^{-8}$  M Rh; (3)  $1.95 \times 10^{-8}$  M Pt; (4)  $1.95 \times 10^{-8}$  M Pt and  $4.86 \times 10^{-8}$  M Rh; initial potential, -0.75 V; drop time, 0.5 s; scan rate, 5  $mvs^{-1}$ ; modulation amplitude, 225 mV.

the electrode process is very complex, and further research is under way.

**Influence of supporting electrolyte composition.** The sensitivity of the waves associated with platinum (A on curve 4) and rhodium (peak C on curve 4) depends on the nature of the acid present. The effect of sulfuric acid concentration on the peak height is shown in Fig. 3. In fact, rhodium complex yields most sensitive peak rather in 0.75 M HCl than in 0.75 M  $H_2SO_4$  where platinum-formazone does, suggesting a mixed type complex formation. Further work on this complex is under way. Overall sensitivities in 0.75 M  $H_2SO_4$  were  $0.6 \mu A/nM$  for Rh and  $0.3 \mu A/nM$  for Pt;  $1.6 \mu A/nM$  for Rh and  $0.08 \mu A/nM$  for Pt in 0.75 M HCl. Sulfuric acid, however, was used throughout this work, because it provides a moderate sensitivity for both of the analytes.

Other conditions that affect the heights of both peaks are the concentrations of formaldehyde and hydrazine. Fig. 4 shows their effects on the rho-

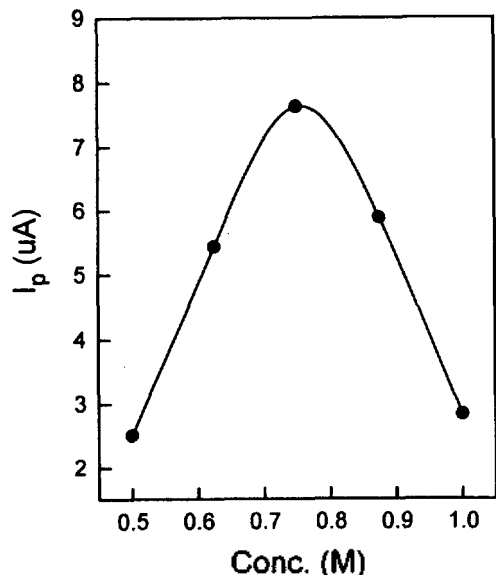


Fig. 3. Effect of sulfuric acid on dpp of  $9.72 \times 10^{-11}$  M Rh(III). Conditions are the same as in Fig. 1, except for the change of sulfuric acid concentration.

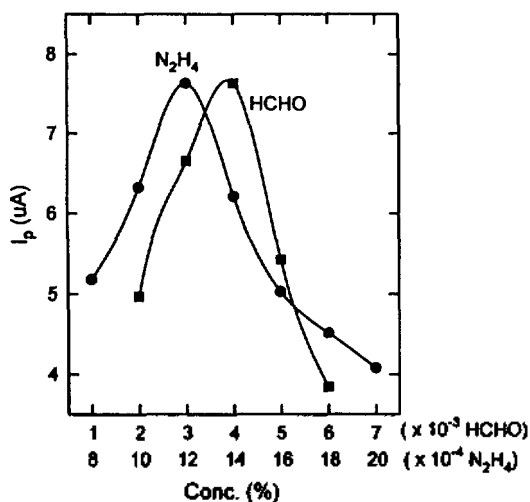


Fig. 4. Effects of formaldehyde and hydrazine on dpp of  $9.72 \times 10^{-11}$  M rhodium. Other conditions are given in Fig. 2.

dium peak. The optimum concentrations for formaldehyde and hydrazine were found to be 0.004% (w/v) and 0.0012% (w/v), respectively. The detection limits ( $3\sigma$ ) of the method are  $7.3 \times 10^{-11}$  M Pt and  $3.2 \times 10^{-11}$  M Rh when each metal ion is present alone, making it one of the most sensitive

Table 1. Influences of rhodium on the simultaneous determination of platinum

Pt conc./M	Rh conc./M	Ratio Pt/Rh	Recovery of Pt/%
$4.88 \times 10^{-10}$	0	1:0	100
	$4.86 \times 10^{-10}$	1:1	98~104
	$9.72 \times 10^{-10}$	1:2	100~105
	$4.86 \times 10^{-9}$	1:10	103~110
	$9.72 \times 10^{-9}$	1:20	105~120
$4.88 \times 10^{-9}$	$1.94 \times 10^{-8}$	1:40	110~130
	0	1:0	100
	$4.86 \times 10^{-9}$	1:1	104~164
	$9.72 \times 10^{-9}$	1:2	100~110
	$4.86 \times 10^{-8}$	1:10	100~110
	$1.94 \times 10^{-7}$	1:40	110~130

Table 2. Effects of platinum on the simultaneous determination of rhodium

Rh conc./M	Pt conc./M	Ratio Rh/Pt	Recovery of Rh/%
$4.86 \times 10^{-10}$	0	1:0	100
	$4.88 \times 10^{-10}$	1:1	100
	$9.75 \times 10^{-10}$	1:2	100~102
	$4.88 \times 10^{-9}$	1:10	100~102
	$9.75 \times 10^{-9}$	1:20	100~102
	$2.93 \times 10^{-8}$	1:60	100~102
$4.86 \times 10^{-9}$	$4.88 \times 10^{-8}$	1:100	100~102
	0	1:0	100
	$4.88 \times 10^{-9}$	1:1	96~100
	$9.75 \times 10^{-9}$	1:2	95~100
	$4.88 \times 10^{-8}$	1:10	98~100
	$2.44 \times 10^{-7}$	1:50	98~100
	$4.88 \times 10^{-7}$	1:100	96~120

methods for trace platinum and rhodium measurement.

**Calibration plot and interference of coexistent ion.** In 0.004% (w/v) formaldehyde-0.0012% (w/v) hydrazine-0.75 M sulfuric acid medium, the peak heights were linear with Pt concentration over the range of  $5 \times 10^{-10}$  M to  $6 \times 10^{-8}$  M and  $1 \times 10^{-10}$  M to  $2 \times 10^{-8}$  M with Rh concentration. The rhodium peak exhibited good reproducibility, while the platinum peak increased to some extent with time. A  $5 \times 10^{-9}$  M Pt solution was determined every 2.5 minutes for 4 times; a 5% increase

in peak current was observed during 10 min (compare to 15% in optimal medium for Pt<sup>2+</sup>) allowing the use of platinum as counter electrode<sup>9</sup> in a simple analytical running.

The interference of some metal ions that might coexist or can interact with the analytes, components of the supporting electrolyte medium was examined. The effects of the common metals were similar to that described previously for platinum<sup>2</sup>. Among PGM ions, Rh<sup>3+</sup> and Ir<sup>4+</sup> interfere with the determination of platinum. The effect of rhodium on the determination of platinum is shown in Table 1. Rhodium and iridium concentrations must be kept under 10 and 100 time that of platinum, respectively. On the contrary, rhodium is not subject to interferences by any of the PGMs, especially by platinum as shown in Table 2.

### CONCLUSION

In a formazone producing medium, platinum gives a single catalytic hydrogen peak (A in Fig. 2, surface catalyzed by Pt-formazone complex); rhodium gives two peaks, peak B and peak C (in Fig. 2) given by Rh-formaldehyde complexes. The wave B is poorly defined to be useful for analytical purposes. Best results with respect to peak shape and overall sensitivity-were obtained with A peak

for Pt and C peak for Rh in 0.004% (w/v) formaldehyde-0.0012% (w/v) hydrazine-0.75 M H<sub>2</sub>SO<sub>4</sub> medium.

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