

# Articles

## Determination of Ultratraces of Rhodium by Adsorptive Stripping Voltammetry of Formaldehyde Complex

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An ultrasensitive and selective stripping voltammetric scheme for the determination of rhodium is described. By the use of combined accumulation and catalytic effects in formaldehyde-hydrochloric acid medium, substantial improvement in the limit of detection can be obtained. Optimal experimental conditions were found to be 0.42 M hydrochloric acid solution containing 0.008% formaldehyde, an accumulation potential of  $-0.70$  V (vs. Ag/AgCl) and an accumulation time of 20 s. The stripping mode was differential pulse voltammetry. In these conditions the limit of detection lies at  $2 \times 10^{-12}$  M (0.21 ppt). The relative standard deviation at  $5 \times 10^{-11}$  M was 4.9% ( $n=5$ ). There were no serious interferences from other platinum group metal ions being the tolerable amounts more than 500 times that of rhodium.

### Introduction

Rapid and highly sensitive methods for the determination of platinum group metals (PGMs) in precious-metal plating baths, certain metallurgical products, fission products of heavy nuclei, pure metals, and semiconductor materials are of interest.<sup>1</sup> For many years, surface-catalyzed proton reduction processes have been used for the polarographic measurement of PGMs. For example, very sensitive catalytic hydrogen polarographic waves are observed for rhodium(III) in the media containing complexing ligands such as, sodium chloride-hydrochloric acid (dynamic range;  $2 \times 10^{-7} - 10^{-5}$  M),<sup>2</sup> cysteine-ammonia buffer ( $2 \times 10^{-9} - 2 \times 10^{-8}$  M),<sup>3</sup> and formazone (formaldehyde-hydrazine)-sulfuric acid<sup>4</sup> media. In the last medium (0.02%(w/v) formaldehyde-0.002%(w/v) hydrazine-0.75 M H<sub>2</sub>SO<sub>4</sub>),<sup>4</sup> dynamic range or limit of detection (LOD) for rhodium was not mentioned. Recently, improvement in detectability (down to  $3.2 \times 10^{-11}$  M Rh(III) even in the presence of Pt(II) in 100-fold) can be obtained by judicious choice of the complexing medium (0.004% formaldehyde-0.0012% hydrazine-0.75 M H<sub>2</sub>SO<sub>4</sub>).<sup>5</sup> In addition, more lowering in LOD, down to  $7 \times 10^{-12}$  M, was achieved in 0.004% formaldehyde (only)-0.75 M HCl medium with differential pulse polarographic (DPP) method.<sup>6</sup> The exceptional sensitivity of this scheme seems to be due to hydrogen ion reduction catalyzed by rhodium-formaldehyde complex. In principle, additional improvement in the LOD for voltammetry can be obtained by preconcentrating the depolarizer. Decrease in the LOD for platinum-formazone complex by two orders of magnitude has been achieved by coupling hydrogen catalytic systems with controlled interfacial accumulation of the catalyst over longer time frame (from  $1 \times 10^{-10}$  M Pt using DPP<sup>4</sup> to  $1 \times 10^{-12}$  M Pt using adsorptive stripping voltammetry for a 30 min preconcentration time<sup>7</sup>). It was therefore expected that analogous lowering in LOD for rhodium could

be achieved.

This work describes an extremely sensitive electroanalytical procedure for ultratrace measurements of rhodium based on adsorptive stripping voltammetry which seems not to have been attempted. It is shown below that the response from the reduction of strongly adsorbed rhodium-formaldehyde complex allows rhodium to be determined down to  $10^{-12}$  M level with a 20 s preconcentration period.

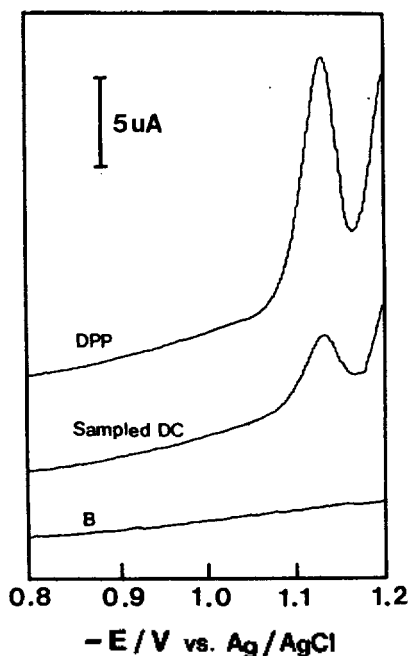
### Experimental

**Apparatus and Reagents.** The sampled DC and differential pulse polarograms, and stripping voltammograms were obtained with an EG & G PAR Model 264 Polarographic Analyzer/Stripping Voltammeter coupled with an EG & G PAR Model 303A SMDE. The detector output was monitored using an EG & G PAR Model RE0088 X-Y Recorder. The cell system consisted of the dropping mercury electrode (DME) with a medium size drop (surface area=0.017 cm<sup>2</sup>) as the working electrode, an Ag/AgCl (saturated KCl) reference electrode and a platinum counter electrode. It was not necessary to remove oxygen from the solution as it does not affect the peak current at all.

All purchased reagent-grade chemicals were used without further purification. Triply distilled mercury in our laboratory was used. The water obtained by passing distilled water through a Milli-Q water purification system was used for diluting and for preparing all solutions.

A 1000 ppm rhodium stock solution (atomic absorption standard, Junsei Co.) was used. Stock solutions of formaldehyde and HCl were prepared daily and stored separately. The required standards were prepared daily by appropriate dilution of the stock solution. Other PGMs were purchased from Aldrich.

**Procedure.** Ten milliliters of the supporting electrolyte



**Figure 1.** Sampled DC and DP Polarograms of rhodium(III) in 0.008%(w/v) formaldehyde  $-0.42$  M HCl ( $2.43 \times 10^{-8}$  M Rh(III)): initial potential,  $-0.700$  V; scan rate,  $5$  mV/sec; modulation amplitude,  $25$  mV; drop time,  $0.5$  s; B, blank of sampled dc.

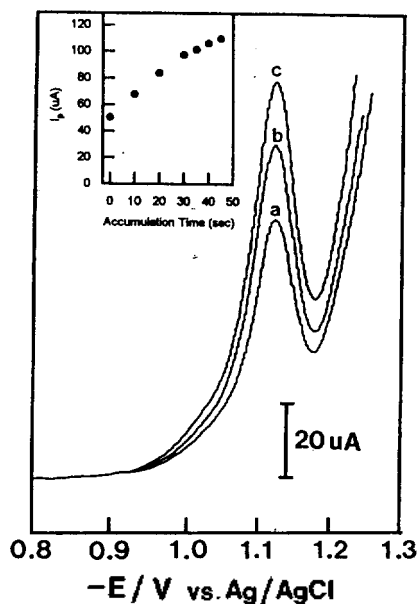
solution, containing 0.008%(w/v) formaldehyde and  $0.42$  M hydrochloric acid were pipetted into the cell.

The accumulation potential was applied to a fresh mercury drop for a selected time, while the solution was stirred at "slow(AUTO)" rate. The stirring was then stopped, and after  $30$  s the voltammogram was recorded from  $-0.7$  to  $-1.3$  V (vs. Ag/AgCl) in differential pulse (DP) mode. After the background voltammogram was obtained, aliquots of the rhodium standards were introduced. Peak currents of the stripping voltammogram were measured in the usual way. All data were obtained at room temperature.

## Results and Discussion

Figure 1 shows sampled DC and DP polarograms (dpp) for  $2.4 \times 10^{-8}$  M rhodium in the presence of 0.008% formaldehyde and  $0.42$  M HCl. The polarograms exhibit well-defined waves that appeared at ca.  $-1.13$  V and  $-1.12$  V (vs. Ag/AgCl), respectively, with characteristic shape of peaks similar to those for Pt-formazone system.<sup>4</sup> As the concentration of rhodium increases to ca.  $5 \times 10^{-7}$  M or more, hydrogen gas bubbles are generated vigorously at the surface of the DME, indicating that the polarographic wave is a catalytic hydrogen wave.

The catalytic wave appears in formaldehyde-HCl medium, leaving little doubt that the polarographically and surface active complex is a formaldehyde (side-on) complex of rhodium.<sup>6,8</sup> Dp stripping voltammograms (dpv) for  $1 \times 10^{-10}$  M rhodium after different accumulation times ( $t_a$ ) at  $-0.7$  V (Figure 2) showed very similar to dpp in shape and peak potential. The adsorption of the rhodium-formaldehyde complex (the catalyst) results in a well-defined catalytic hydrogen peak at  $-1.12$  V, with a substantially larger current. For



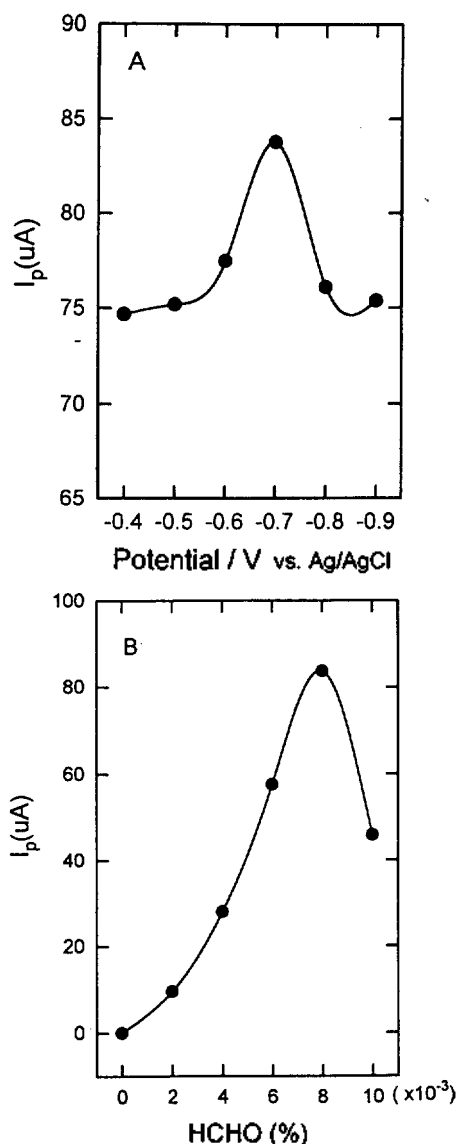
**Figure 2.** Differential pulse adsorptive stripping voltammograms for  $9.7 \times 10^{-11}$  M rhodium after different accumulation times: (a)  $10$  s; (b)  $20$  s; (c)  $30$  s; preconcentration potential,  $-0.700$  V. The inset shows the resulting current/time plot. Other conditions were as in Figure 1.

example, a  $20$  s preconcentration time yielded a 1500-fold enhancement of the peak current compared to dpp (sensitivity from  $0.57$  to  $862$   $\mu\text{A/nM}$ ).

The dependence of the current on the preconcentration time was linear up to  $30$  s, and then started to deviate downward (Figure 2 inset), with large initial current ( $t_a=0$ ). For  $\geq 50$  s the dpv disappeared completely. The large initial current and narrow linear range of preconcentration time compared to conventional cases ( $60$ - $1800$  s) indicate that the rhodium-formaldehyde complex is adsorbed rapidly and strongly on the mercury surface. Further research on this concern is under way. For the wide linear dynamic range of rhodium, an accumulation time of  $20$  s was preferred for all subsequent work.

The dependence of the current on the preconcentration potential was examined over the  $-0.40$  to  $-0.90$  V range. Hence, optimal conditions are obtained at  $-0.70$  V (Figure 3A). Figure 3B shows the influence of the formaldehyde concentration on the adsorptive/catalytic response. The response increased gradually upon increasing the ligand concentration from zero to  $0.01\%$ , following which a sharp decrease in the response was obtained. At  $0.008\%$  formaldehyde, a doubled value for dpp ( $0.004\%$ ),<sup>6</sup> the optimal conditions were obtained.

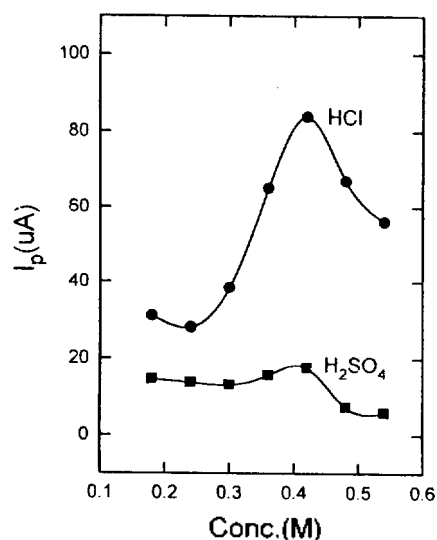
To obtain the catalytic hydrogen current, high acid concentration should be used. Chemical problems, associated with the use of other acid than sulfuric acid as a supporting electrolyte, were discussed for the Pt-formazone-sulfuric acid scheme.<sup>4</sup> Unlike the Pt-formazone case<sup>4,7</sup> a preference of hydrochloric acid over sulfuric acid with a somewhat lower concentration is obvious from Figure 4. Hence, optimal conditions were obtained at  $0.42$  M hydrochloric acid, suggesting that the depolarizer is likely a mixed complex of formaldehy-



**Figure 3.** Effect of preconcentration potential (A), and formaldehyde concentration (B) on the stripping peak current. Rhodium concentration:  $9.7 \times 10^{-11}$  M. Accumulation time: 20 s. Other conditions were as in Figure 2.

de and chloride.

With the optimized conditions, a linear dynamic range was evaluated by varying the rhodium concentration from  $9.72 \times 10^{-12}$  M to  $9.72 \times 10^{-10}$  M. Good linear calibration curves are observed (not shown), with a slope of  $163 \mu\text{A nM}^{-1}$  (correlation coefficient: 0.998). The relative standard deviation ( $n=5$ ) in this linear dynamic range was 5.1%. The LODs were estimated from measurements of  $9.72 \times 10^{-12}$  M rhodium, with 20 and 30 s preconcentration. Calculated (from  $3\sigma$  ( $n=10$ )) values were found to be  $1.1 \times 10^{-12}$  M ( $t_a=30$  s) and  $2.0 \times 10^{-12}$  M ( $t_a=20$  s). These values mean that in the 10 mL of solution used, 1.1 or 2.1 pg can be detected. To the best of our knowledge, the LODs obtained in the present work are the lowest reported, for a such short preconcentration period, for any analyte by voltammetric method.



**Figure 4.** Effect of  $\text{H}_2\text{SO}_4$  and HCl and their concentration on the stripping peak current. Conditions were the same as in Figure 3, except for the change of acid concentration.

Interference from coexisting metal ions and surface-active substances were evaluated. In the presence of Triton X-100 ( $3 \times 10^{-5}\%$ ) the current diminished to ca. 60% of its original value. Only metals yielding catalytic peaks at similar potential or reacting with formaldehyde or rhodium, are expected to interfere. As expected, measurements of rhodium by the present scheme were not affected by most heavy or transition metals. There are no serious interferences from other PGM ions.

In conclusion, the present study describes an analytical method based on accumulation and catalytic effects of rhodium that provides the lowest detection limit ever reported by voltammetric method. More work is desired to identify the complex and to obtain better understanding of the nature of the adsorption and catalytic process.

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