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벗김 전압전류법에 의한 루테늄의 미량 측정

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Trace Measurement of Ruthenium by Adsorptive Stripping Voltammetry

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요 약. 히드록실아민이 존재하는 붕산염 매질에서 루테늄(III)은 수은 표면에 사전농축이 잘 되었고 이 피흡착질의 환원 생성물에 의한 촉매 수소 전류를 측정함으로써 흔적량 루테늄을 간편하게 정량할 수 있었다. 순환 전압전류법으로 산화환원 및 흡착 누적 특성을 조사하였다. 최적 조건은 다음과 같다: 붕산염 0.015 M, pH 2.5, 히드록실아민 0.55 M, 누적 전위 −0.70 V, 그리고 시차 펄스 모드에서 주사속도 5 mV/s이었다. 이 조건에서 검출한계는 3×10^{-10} M(7분 수집)이었다. 방해 가능한 다른 백금족 금속이온들의 허용량도 조사하였다.

ABSTRACT. In the presence of optimum amounts of hydroxylamine, trace ruthenium(III) can be conveniently determined in acidic (boric) media by coupling catalytic hydrogen processes with adsorptive accumulation of the catalyst, using differential pulse voltammetry. Cyclic voltammetry was used to characterize the redox and interfacial processes. Optimal experimental conditions were found to be a stirred borate (0.015 M, pH 2.5) solution containing 0.55 M hydroxylamine, a preconcentration potential of −0.70 V, and a scan rate of 5 mV/s. With a 7 min accumulation period the detection limit was 3×10^{-10} M. The possible interferences by other platinum group metals are investigated.

INTRODUCTION

Because of the importance of ruthenium, a simple and highly sensitive method for its determination is required. Catalytic kinetic method[1] has been demonstrated to be a sensitive analytical method for various platinum metals. Especially for ruthenium, this homogeneous kinetic method offers the most sensitive scheme when the method was coupled with single-sweep oscillopolarographic method (detection limit, 3 pM).[2,3] Such a sensitivity, however, can only be attained when strict experimental conditions are fulfilled. The simple and convenient procedure with satisfactory sensitivity is prompted by the limitations involved in performing catalytic (homogeneous) kinetic experiment.

Measurements of catalytic (EC')[4,5] and catalytic hydrogen currents[6,7] have been reported for the determination of trace amounts of ruthenium, but their sensitivity is not satisfactory (at the best 2×10^{-7} M). Recently, improvement in detectability (down to the 5×10^{-8} M level) can be obtained by coupling the adsorptive accumulation of ruthenium complexes with differential pulse measurements.[8] For many years, catalytic hydrogen voltammetry with adsorptive accumulation has been used for trace measurements of some platinum-group metals. For example, platinum[9] with detection limit of 1.2×10^{-12} M (30 min preconcentration), rhodium[10]

with 2×10^{-12} M (20 s preconcentration), and ruthenium[11] with 2×10^{-9} M (7 min preconcentration).

This work describes an elaborated scheme for the trace measurement of ruthenium by which the detection limit can be lowered an order of magnitude, 3×10^{-10} M with 7 min accumulation.

EXPERIMENTAL

Apparatus and reagents. All stripping and cyclic voltammetric (cv) experiments were carried out using an EG&G PAR Model 264 polarographic analyzer and Model 362 scanning potentiostat respectively, in connention with an EG&G PAR Model 0089 X-Y Recorder. All experiments were performed at laboratory temperature (25±2 ℃) by using a standard three-electrode, one compartment configuration with a PAR Model 303 static mercury drop electrode (area: 0.017 cm^2), as the working electrode, a spiral platinum counter electrode and a KCl saturated Ag/AgCl reference electrode. Solutions were deoxygenated with Ultra-pure carrier grade nitrogen gas (Hankook Sanup gas) for 4 min prior to each experiment and all experiments were performed under a nitrogen atmosphere.

Water purified in a Milli-Q Plus water purification system (Millipore) was used throughout the experiments. A 1000 ppm rutheniun stock solution containing 5 wt% HCl (atomic absorption standard, Aldrich) was used. All other platinum-metal solutions also were atomic absorption standard; osmium (Fluka), iridium (Aldrich), rhodium and platinum (Junsei). Hydroxylamine and borax were obtained from Aldrich.

Procedure. Ten milliliters of the supporting electrolyte solution, containing borax (0.015 M) and hydroxylamine (0.55 M) were pippeted into the cell, and deoxygeneated with nitrogen for 4 min. The preconcentration potential (usually −0.70 V) was applied to a fresh mercury drop for a selected time, while the solution was stirred (at auto slow). The stirring was then stopped, and after 30 s the voltammogram was recorded by applying either a linear potential scan to −1.2 V (cv) or differential pulse with a scan rate 5 mV/s (stripping). After the background voltammogram was obtained, aliquots of the ruthenium standards were introduced. The solution was stirred and purged for 2 min. The cv or adsorptive stripping cycle was repeated using a new mercury drop. The settings in differential pulse mode were: pulse amplitude, 25 mV; drop time, 0.5 s.

RESULTS AND DISCUSSION

Fig. 1 shows typical cyclic voltammograms for differing conditions. The adsorption of the ruthenium/hydroxylamine complex results in a well-defined catalytic hydrogen peak at −0.94 V (curve b). This peak increases with increasing preconcentration time, for example, a 3 min accumulation period yielded a 7.5-fold enhancement relative to that obtained without preconcentration (compare b and d). Repetitive cyclic voltammograms (curve c) showed a similar response (other conditions as in curve b). The first scan (designated

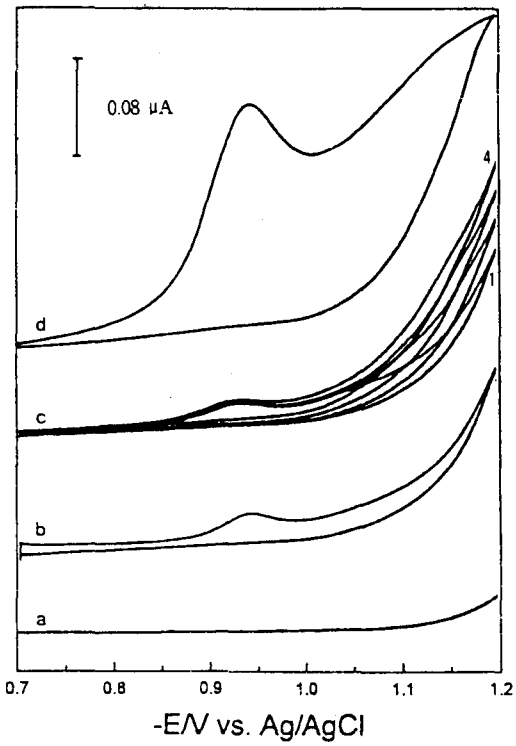


Fig. 1. Cyclic voltammograms for (a) 0.015 M borate + 0.55 M hydroxylamine (pH 2.5), (b) (a) $+1.45\times10^{-7}$ M Ru, (c) repeatitive (b), and (d) same as (b) after preconcentration for 3 min at −0.70 V. Scan rate 10 mV/s.

as 1) and subsequent scans yield almost equal and stable cathodic peaks, indicating a rapid desorption of the catalyst from the surface. This rapid desorption means earlier termination by disproportionation in a catalytic chain reaction, in the sense of Brdicka currents,[12] compared to the cases of platinum/formazone[9] and rhodium/formaldehyde[10] where desorption of the catalyst was shown to be gradual and consequently yielded lower detection limits (picomolar level). Mechanistic complexities, associated with the varying characteristics of catalytic hydrogen currents with the identity of the catalyst and experimental conditions, were discussed elsewhere.[12,13]

Numerous solution conditions and instrumental parameters affecting the ruthenium response were evaluated and optimized. The effects of different kinds of supporting electrolytes were evaluated by using other buffers, such as Britton-Robinson,[4] KCl-HCl,[6] acetate, and phosphate buffers, than borate buffers as supporting electrolyte. The sensitivities from the calibration graphs (not shown) obtained over the $1\sim10\times10^{-8}$ M ruthenium range were 1.69 ± 0.06, 0.52 ± 0.02, 0.32 ± 0.06, 0.17 ± 0.02, 0.09 ± 0.01 μA/10 nM for 0.015 M borate, 0.02 M KCl-0.005 M HCl, 0.015 M acetate, 0.015 M phosphate, and 0.015 M Britton-Robinson buffer, respectively (other conditions as in *Fig.* 1). These data indicate that borate medium offers the most sensitive result.

The effect of the borate concentration was evaluated over the 0.0~0.03 M range (*Fig.* 2). The peak current increased rapidly, without any changing in peak shape, upon increasing the borate concentration from 0.00 to 0.015 M, following which a sharp decrease in the response was observed. Hence, optimal conditions were obtained at 0.015 M over which boric acid, as a Lewis acid, rather competes with proton for the catalyst in the protonation step than supplies proton. Also shown in *Fig.* 2 is the dpendence of the peak potential on borate concentration. A negative shift of ca. 30 mV per decade change in borate concentration (from 0.001 to 0.01 M) was observed.

Other solution conditions affecting the adsorptive/catalytic response include the level of hydroxylamine and pH. The peak curent increases in proportion to the square root of the hydroxylamine concentration (*Fig.* 3A inset) up to about 0.05 M, indicating the current increase is due to the EC' catalytic process.[4] With further increase in hydroxylamine concentration, however, the current variation appeared in a peak shape with a maximum at 0.55 M (*Fig.* 3A). Increasing the solution pH from 2.0 to 7.0 resulted in a rapid increase of the peak height; a sharp decrease in the response was observed at pH>2.5 (*Fig.* 3B).

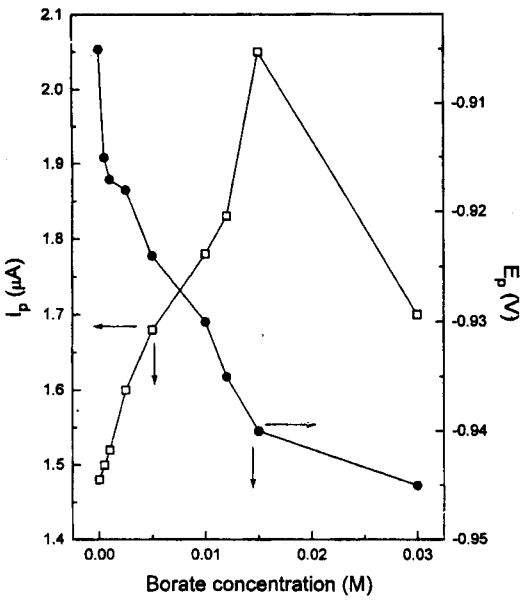


Fig. 2. Effects of the borate concentration on the peak current (□) and peak potential (●). Other conditions are the same as in *Fig.* 1.

The dependence of the current on the preconcentation potential was examined over the -0.40 to -0.80 V range. A rapid increase to a maximum current value at -0.70 V after which a sharp decrease was observed (*Fig.* 4A). Optimal conditions included 0.55 M hydroxylamine solution (pH 2.5) containing 0.015 M borate, and preconcentation at -0.70 V. The differential-pulse waveform yielded better signal-to-noise characteristics than the linear scan stripping mode. When optimizing the preconcentration time, a trade-off between sensitivity and speed would be required. *Fig.* 4B shows the plots

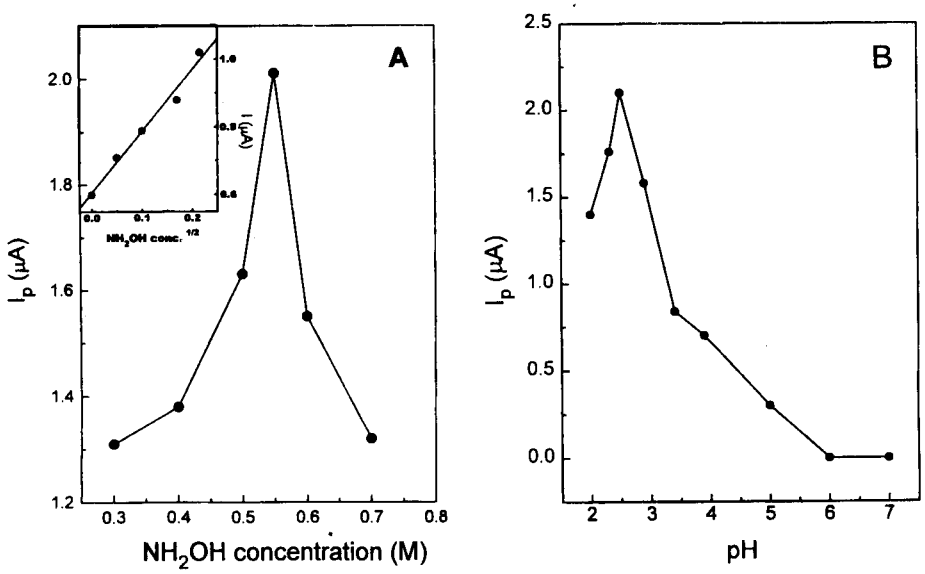


Fig. 3. Dependence of peak current on (A) hydroxylamine concentration and (B) pH. Conditions are the same as in *Fig.* 1.

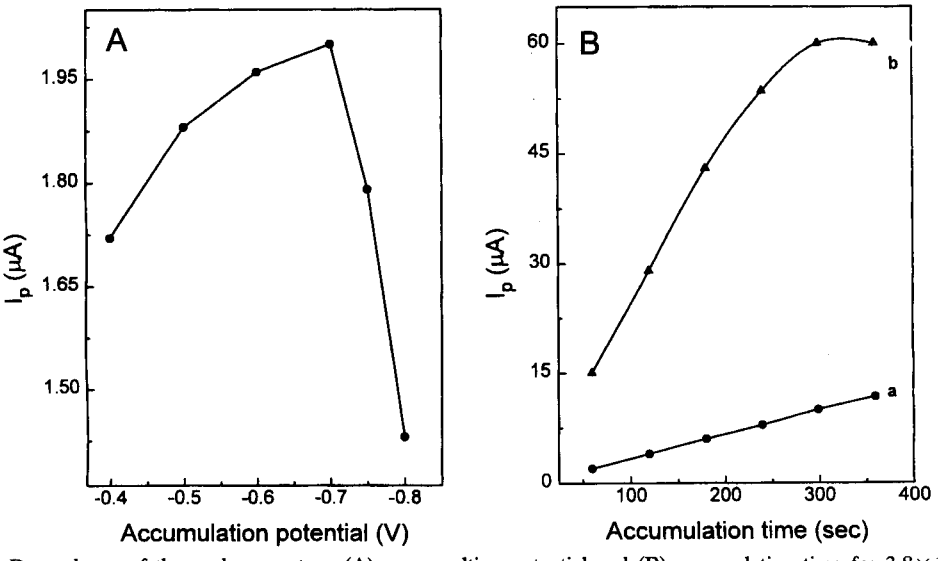


Fig. 4. Dependence of the peak current on (A) accumualtion potential and (B) accumulation time for 3.8×10^{-8} M (a) and 3.8×10^{-7} M Ru(b). Other conditions, as in *Fig.* 1.

of peak current *vs.* preconcentration time for two diffrent ruthenium concentrations. As expected for processes limited by adsorption of the analyte, deviations from linearity are obtained at the higher concentrations. Times of 60 s and 180 s suffice for convenient quantitation of ruthenium at the 3.8×10^{-7} M and 3.8×10^{-8} M levels, respectively. Detection limits were estimated from measurements of 3.9×10^{-9} M ruthenium, following 3 and 7 min preconcentration and resulted 8.0×10^{-10} M and 2.9×10^{-10} M, respectively. *Fig.* 5 shows stripping voltammograms obtained after increasing the ruthenium concentration in 10 nM steps (a-c), following 3-min preconcentration. These three measurements are part of ten increments with which the calibration plot resulted as shown (inset). Linear

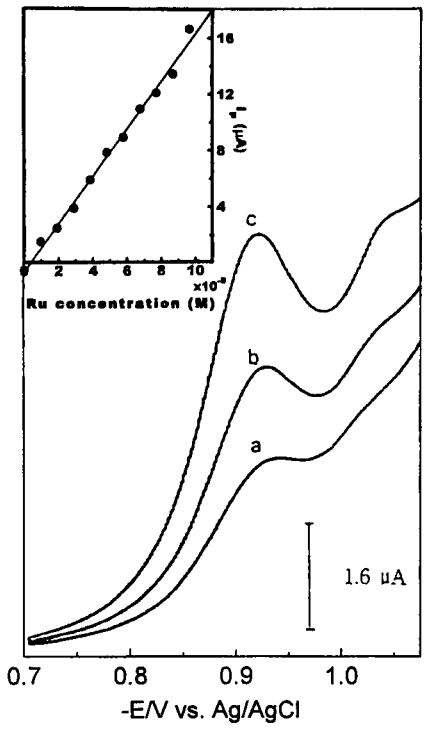


Fig. 5. Stripping voltammograms for solutions of increasing ruthenium concentration, $1.9\sim3.9\times10^{-8}$ M (a~c). Other conditions, as in *Fig.* 1. Inset: The resulting calibration plots, over $0.97\sim9.7\times10^{-8}$ M, with calculated (least-square) $I_p(\pm0.05)=\{(1.69\pm0.06)\times10^{8}\}C-0.56(\pm0.34)$.

calibration curve is observed, with slope of 0.170 μA/nM (correlation coefficient: 0.998). The reproducibility of the data was estimated from two series of measurements performed at different ruthenium concentrations. Ten successive measurements of 9.7×10^{-9} and 9.7×10^{-8} M ruthenium yielded relative standard deviations of 1.3 and 0.30%, respectively (mean peak current, 1.56 and 16.6 μA, respectively). With 3 min of preconcentration time the linear dynamic range was $4.8\times10^{-9}\sim4.8\times10^{-7}$ M.

Catalytic waves and adsorptive stripping peaks are frequently affected seriously by the presence of organic surfactants. Such material could be interfered by competing with the catalyst on adsorption sites. Triton X-100 at 0.5, 1, and 2 mg L^{-1} (3.2×10^{-8} M ruthenium, 3 min preconcentration) resulted in 20, 43, and 45% depressions, respectively, of the initial ruthenium response.

Only metals yielding catalytic peaks at a similar potential are expected to interfere. The effects of various platinum-group metals on 4.8×10^{-8} M ruthenium response were investigated for 3 min preconcentration. Minor changes (<10%) in the response were observed in the presence of 10, 3, 2, and 1 times the concentration of ruthenium for Ir (IV), Os(IV), Rh(III), and Pt(IV). respectively. Os and Ir yielded positive and Pt and Rh negative effects.

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