DIFFERENTIAL PULSE POLAROGRAPHIC DETERMINATION OF OSMIUM BY CATALYSIS OF PYROGALLOL-RED BROMATE REACTION

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Abstract

A highly sensitive differential pulse polarographic (DPP) method has been developed for the determination of trace amounts of osmium, based on the catalytic effect of osmium (VIII) on the oxidation of pyrogallol red (PGR) by sodium bromate at pH 7.00 and 25.0 ± 0.1 °C. The reaction rate was monitored by measuring the differential pulse cathodic current of the oxidation product of PGR and bromate. Various parameters such as the effect of pH, reagents concentrations, time, temperature and interference of a number of cations and anions on the estimation of osmium have been studied to optimize the conditions for determination of osmium. The concentration of osmium in the range of 0.1-300 ng ml^{-1} has been determined. The limit of detection was 0.02 ng ml^{-1}. The precision and accuracy of the method are reported.

Introduction

Pyrogallol red (PGR) oxidations by means of kinetic studies have been used for the determination of several species. Determination of trace amounts of lead [1, 2], iodide [3], vanadium [4, 5], silver [6], cerium (IV) [7] based on their catalytic effects on the oxidation of PGR by potassium peroxodisulfate, hydrogen peroxide and potassium bromate has been reported.

A survey of the literature reveals that osmium may be determined in different samples using spectrophotometric methods [8-14]; x-ray fluorescence spectrometry [15]; potentiometry [16-18]; atomic absorption and fluorescence spectrometry [19-22]; atomic emission spectrometry [23]; and oxidation reduction reactions [24, 25]. The poor selectivity and sensitivity of many existing techniques have necessitated the development of adequate separation and preconcentration procedures. Even atomic spectrometric techniques are not free from interferences [20-22].

Catalytic kinetic methods are very sensitive in the

determination of osmium [26-36], but there is no report on the kinetic polarographic determination of osmium based on the catalytic oxidation of PGR.

In the present communication, we have developed a sensitive method for the differential pulse polarographic determination of osmium based on its catalytic effect on the oxidation of pyrogallol red by sodium bromate. Various parameters such as pH, pyrogallol red and bromate concentrations, time, temperature, instrumental parameters and interference of a number of cations and anions on the estimation of osmium have been evaluated. Possible interferences could be eliminated by the distillation of osmium tetroxide [37] or by using extraction methods [38]. The preconcentration of osmium is also possible using an appropriate extraction method.

Experimental Section

Reagents

All chemicals were analytical grade from Merck (Darmstadt, Germany). Deionized double distilled water was used throughout the measurements.

A standard solution of osmium was prepared by dissolving 0.5 g of osmium tetroxide in about 50 ml of 0.20

M sodium hydroxide solution in a glass stoppered 500 ml volumetric flask and diluted to the volume with water. The solution was standardized iodometrically [39]. Sodium bromate (NaBrO$_3$) solution (0.52 M) was prepared by dissolving 39.23 g of the salt in water and diluting to 500 ml. Pyrogallol red solution (7.20×10^{-4}M) was prepared by dissolving 0.0288 g of PGR in methanol and diluting to 100 ml in a volumetric flask. The solution is suitable for at least a month. A buffer solution of pH 7.00 was prepared from potassium dihydrogen phosphate (0.10 M) and sodium hydroxide (0.10 M) using a pH meter.

All of the stock solutions (1000 μg ml^{-1}) of interfering ions were prepared in water using suitable salts. Potassium chloride (1.00 M stock solution) was used as the supporting electrolyte. Working solutions of osmium tetroxide and interfering ions were prepared shortly before use.

Apparatus

All polarographic measurements were performed on a Model Polarecord E506 Polarograph equipped with a E505 Stand (Metrohm Herisau, Switzerland) using a three electrode system (dropping mercury electrode, Ag/AgCl reference electrode and auxiliary Pt electrode). A Corning Model 125 Digital pH Meter (Corning, Medfield Ma., U.S.A.) was used for measuring the pH of solutions. The measuring cell was thermostated at 25.0±0.1°C using a Haake Model FK2 (Haake, Karlsruhe, Germany) circulation water bath.

Results and Discussion

Polarographic investigation of different solutions containing PGR, PGR-bromate and PGR-osmium (at ng osmium concentrations) show no detectable DPP peak in the potential range of 0.0 to -1.0 V (vs. Ag/AgCl). However, PGR-bromate solutions at ng osmium concentrations show a polarographic current which depends on the concentration of osmium. Typical DPP polarograms and the corresponding working curve in the range of 20-150 ng ml^{-1} of osmium (VIII) are shown in Figures 1 and 2, respectively. Such a polarographic current could also be observed at relatively high concentrations of osmium (at μg levels), even in the absence of sodium bromate.

According to the above observations, the polarographic current could be observed if a relatively large concentration of Os (VIII) is available for oxidation of PGR, or osmium (VIII) is catalytically regenerated via the reaction with bromate. Further, it may be concluded that PGR is oxidized by Os (VIII) and the observed polarographic current is the result of reduction of the oxidized form of PGR. These observations suggest the presence of a catalytic current [34, 40, 41].

Polarographic investigation of the PGR-bromate-osmium system shows that there is a direct dependence of
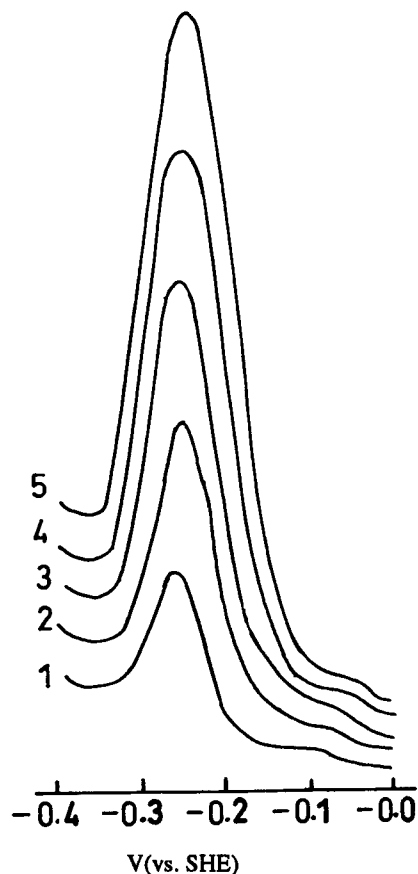

Figure 1. Differential pulse polarograms of PGR- bromate-osmium at 20.0, 50.0, 75.0, 90.0 and 150.0 ng/ml of osmium, Plots 1 to 5, respectively
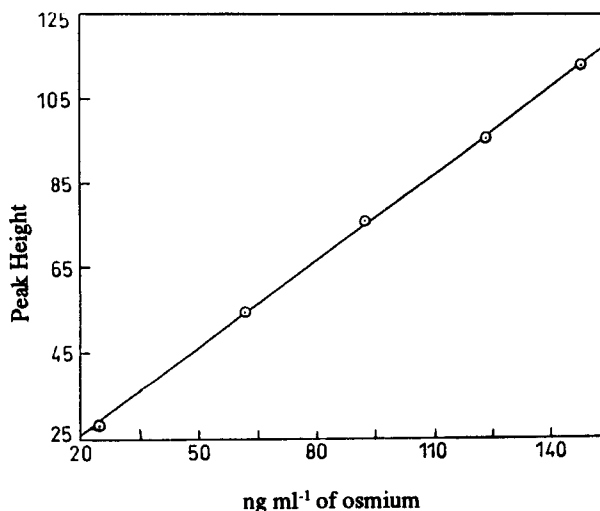

Figure 2. Effect of osmium concentration, 20.0-150.0 ng ml^{-1} on the rate of PGR-bromate reaction at the optimized conditions

DPP current on h (height of mercury column) and $t^{3/2}$ (mercury drop time), and a positive shift was observed in the reduction potential upon increasing the concentration of osmium. These observations also suggest the presence of a catalytic reaction [42].

The effects of single factor optimization of different parameters are given in the following sections.

Effect of pH

This study was made over the pH range 5.00-8.00 using phosphate buffers. There was no detectable polarographic peak at pH<5. By increasing the pH to 7.5, the reaction rate was increased. At pH>7.5, PGR was not stable, and decolorization of the reagent was observed. Therefore, a pH of 7.00 was used during the measurements as the optimum working pH. The effect of pH on the oxidation rate of PGR with sodium bromate in the presence of 1.50 ng ml^{-1} osmium (VIII) as osmium tetroxide is shown in Figure 3.

Effects of Concentrations of Bromate and PGR

The influence of sodium bromate concentration in the range of 0.005 - 0.3 M was studied on solutions containing PGR (3.60 × 10^{-5} M), potassium chloride (0.20 M), osmium tetroxide (1.50 ng ml^{-1} as Os) at pH 7.00 and 25.0 °C. By increasing the concentration of sodium bromate to 0.10 M, there was a sharp increase in the DPP peak height (Fig. 4). At higher bromate concentrations, a slow increase in the reaction rate was observed. Therefore, a final bromate concentration of 0.10 M was chosen as the working concentration.

The effect of PGR concentration on the reaction rate was studied on solutions containing 0.10 M sodium bromate, 0.20 M potassium chloride, 1.50 ng ml^{-1} osmium and different PGR concentrations in the range of 1.0 × 10^{-5} -

1.0 × 10^{-4} M. Other conditions were the same as above. By increasing the concentration of PGR to 3.60 × 10^{-5} M, there was an increase in the reaction rate (Fig. 5). At higher PGR concentrations, the DPP current is decreased, which is probably due to a change of reaction order. Therefore, a final 3.60 × 10^{-5} M PGR was used as the optimized concentration.

Effect of Temperature

This study was made in the range of 10-40°C on solutions containing 3.60 × 10^{-5} M PGR, 0.10 M sodium bromate, 0.20 M potassium chloride at pH 7.00 and in the presence of 1.50 ng ml^{-1} osmium as osmium tetroxide. The
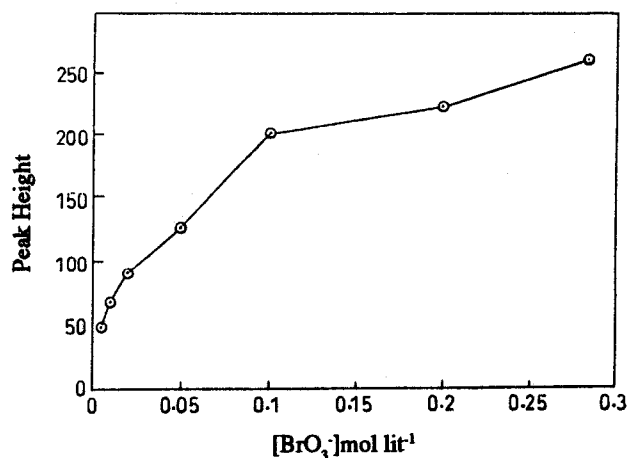

Figure 4. Effect of bromate concentration on the DPP behavior of PGR-bromate-Os system. Conditions: PGR, 3.60 × 10^{-5} M; KCl, 0.20 M; OS (VIII), 1.50 ng ml^{-1}; pH, 7.0
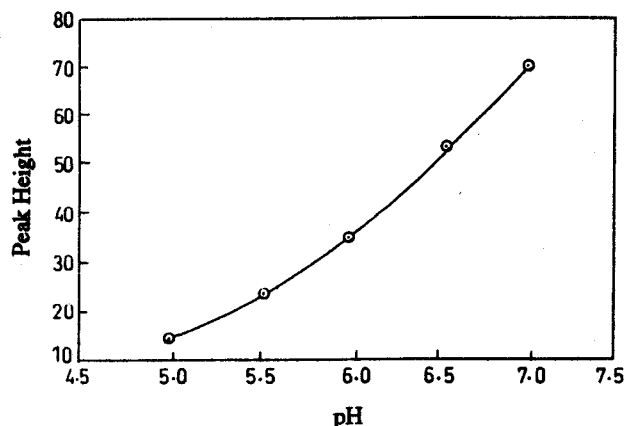

Figure 3. Effect of pH on the DPP behavior of PGR-bromate-Os system. Conditions: PGR, 3.60 × 10^{-5} M; bromate, 0.05 M; Os (VIII), 1.50 ng ml^{-1}; T, 25.0°C

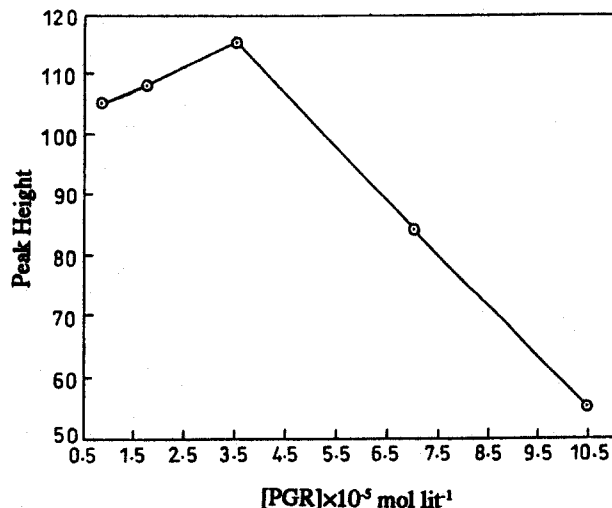**Figure 5.** Effect of PGR concentration on the DPP behavior of PGR-bromate-Os system. Conditions: bromate, 0.10 M; KCl, 0.20 M; Os (VIII), 1.50 ng ml^{-1}

effect of temperature on the rate of reaction is shown in Figure 6. For the sake of simplicity, all measurments were carried out at 25.0°C.

Effect of Instrumental Parameters

The effect of some instrumental parameters such as pulse amplitude and mercury drop time was investigated. As was expected, by increasing the pulse amplitude, peak height was also increased. Therefore, the maximum possible pulse amplitude was used during the measurements.

The effect of mercury drop time is shown in Figure 7. By increasing the lifetime of mercury drop in the range of 0.4- 4 seconds peak heights were increased. This increase was very sharp up to 1.2 s. Therefore, a drop time of 1.2 s was used for measurements.

Effect of Measuring Time

Time was measured just after the addition of the last drop of PGR solution. The effect of time on the sensitivity of the measurements is shown in Figure 8. From the results of this study, for all of the measurements, scanning of the polarogram was started exactly 1.0 min after the addition of the PGR solution, which corresponds to about 2 min in Figure 8.

Calibration

Under the optimized conditions described above, calibration curves were obtained by applying the fixed time method. The oxidation rate of PGR is a linear function of osmium concentration. This linearity was obtained under the following conditions: with osmium concentrations of 0.10-5.0 ng ml^{-1} at -0.736 V peak

potential (vs. Ag/AgCl) (r=0.9992, n=5, n=number of data points). At osmium concentration of 20.0- 300.0 ng ml^{-1}, the peak height at -0.435 V (vs. Ag/AgCl) was a linear function of osmium concentration (at 20-150 ng ml^{-1} of osmium, r= 0.9998, n= 5 and at 150-300 ng ml^{-1} of osmium, r= 0.9992, n=5). In the range of 5-20 ng ml^{-1} of osmium, the peak height at -0.736 V was a second order function of osmium concentration.

### Precision and Limit of Detection

Under the optimized conditions, the precision of the method was evaluated using eight independent solutions
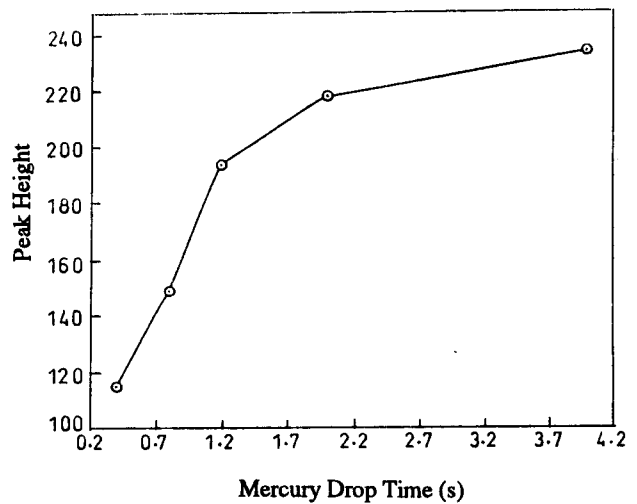
Figure 7. Effect of mercury drop time on the DPP behavior of PGR-BrO_3-Os system. Conditions: PGR, 3.60×10^{-5} M; $NaBrO_3$; 0.10 M; Os (VIII), 1.50 ng ml^{-1}; pH, 7.0; T, 25.0°C
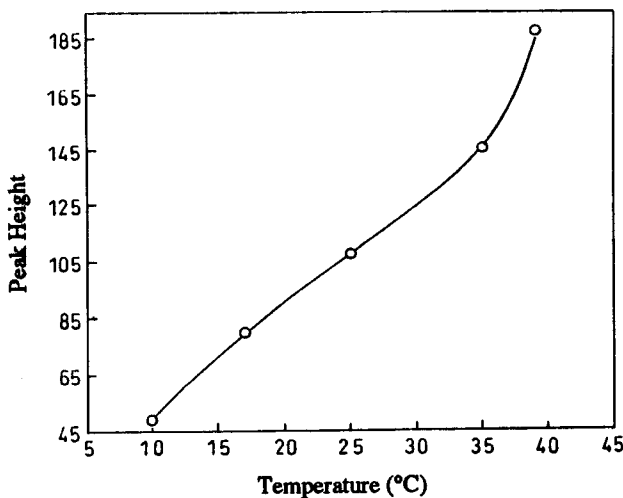
Figure 6. Effect of temperature on the DPP behavior of PGR-bromate-Os system. Conditions: PGR, 3.60×10^{-5} M; $NaBrO_3$, 0.10 M; KCl, 0.20 M; Os (VIII), 1.50 ng ml^{-1}; pH, 7.0
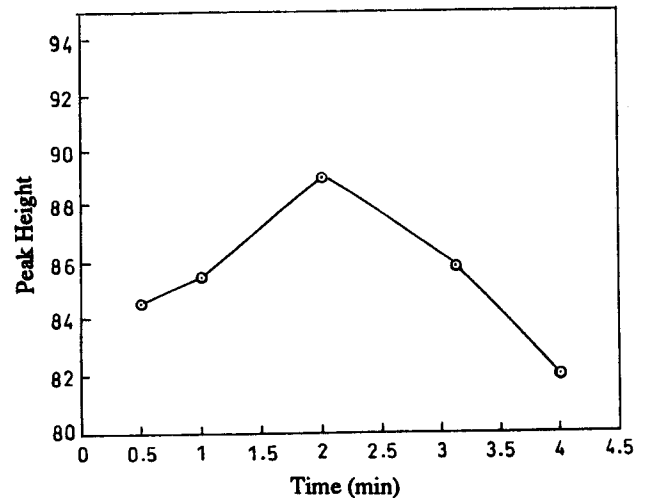
Figure 8. Variation of DPP peak heights of PGR-BrO_3-Os system with time. Conditions: PGR, 3.60×10^{-5} M; $NaBrO_3$, 0.10 M; Os (VIII), 1.50 ng ml^{-1}; pH, 7.0; T, 25.0°C

Table 1. Precision of the method at the optimized conditions

Conc. of osmium ng ml⁻¹	Mean conc. of osmium ng ml⁻¹ n=5	Standard deviation ng ml⁻¹
0.85	0.87	0.06
3.00	3.03	0.07
9.50	9.55	0.05
16.00	15.97	0.05
61.00	60.99	0.09
123.0	123.0	0.10
190.0	190.0	0.11
260.0	260.0	0.09

of various concentrations of Os and fixed concentrations of PGR and bromate. The results of five replicate measurements on each sample are presented in Table 1. The osmium concentration in each case was calculated by substituting the peak height into the corresponding equation for the calibration graph. For osmium concentrations greater than 2 ng ml⁻¹, the relative standard deviation was in the range of 0.03-2%. The theoretical limit of detection $(Y_{L.D.}=Y_B+3S_B)$ [43] for this study was 0.02 ng ml⁻¹ of osmium.

Interference Study

The influence of 47 species on the oxidation of 3.60×10^{-5} M PGR in the presence of 0.10 M NaBr O_3 and 3.0 ng ml⁻¹ of osmium was studied. The polarograms of the solutions were obtained in the absence and in the presence of the foreign ions. The results are given in Table 2, where

Table 2. Effect of foreign ions on the determination of 3.0 ng ml⁻¹ of osmium at the optimized conditions. Tolerance limit was taken as the molar ratio of Ion/Os causing less than ±2% relative error in osmium recovey.

Ion added	Tolerance limit
Al (III), Bi (III), Ba (II), Ca (II), Mg (II), Sr (II), Li(I), Tl(I), F⁻, Br⁻, CH₃COO⁻, ClO_3^-, SO_3^{2-}, SO_4^{2-}, $S_2O_8^{2-}$	1000
As (V), Au (III), Cr (III), Pb (II)	500
Ce (III), Cu (II), Ni (II), Pd (II), I⁻, IO_3^-, ClO_4^-, SCN⁻	200
W (VI), Zr (IV), As (III), IO_4^-	100
Cr (VI), Ce (IV), Co (II), Mn (II), Ag (I), Cd (II), $S_2O_3^{2-}$	50
Mn (VII)	20
Fe (III), Zn (II)	10
Mo (VI)	5
V(V), Fe (II), Sn (II)	3
CN⁻	2

the maximum tolerance limit for each ion was taken as the amount required to cause more than ± 2% error in osmium recovery.

The following extraction technique was used for separation of osmium from interfering species [38]. A series of solutions containing 200 ng ml⁻¹ of Os (VIII) and 0.1 mg ml⁻¹ of the interfering ions were extracted into an equal volume of isobutyl methyl ketone (IBMK) at pH 7.0. Osmium in the organic phase was back extracted into 0.5M sodium hydroxide solution and the resulting solution was used for the determination of osmium by DPP at the optimized conditions. A recovery of 100 ±1% was found for these samples with standard deviations of less than 2%.

Recommended Procedure

In a 25 ml volumetric flask, introduce an appropriate aliquot of sample (not more than 5 ml) to give a final concentration of 0.1-300 ng ml⁻¹ osmium, 5.0 ml potassium chloride (1.00 M), 5.0 ml of sodium bromate (0.520 M) and 5.0 ml of pH 7.00 buffer solution. Dilute the solution to the volume with water. Transfer 20.0 ml of the solution to the polarographic cell and deaerate for 10 min with an inert gas. Keep the temperature of the cell at 25.0°C. Add 1.0 ml of PGR solution (7.20 ×10⁻⁴M), previously brought to the same temperature, to the cell and deaerate for one more min. Measure the time just after the addition of the PGR solution and after 1 min record the polarogram from -0.4 to -0.8 V at 100 mV pulse amplitude and mercury drop time of 1.2 s.

Conclusion

This catalytic differential pulse polarographic method is highly sensitive and is recommended for the determination of osmium at concentration levels as low as 0.1 ng ml⁻¹ with a good precision. This procedure has been used satisfactorily for the analysis of laboratory samples in the presence of interfering substances.

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