



Application of Thionine Dye for Highly Sensitive and Selective Catalytic Kinetic Determination of Osmium

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ABSTRACT

A new, highly sensitive and selective catalytic kinetic method (CKM) for determination of osmium (VIII) has been established based on its catalytic effect on the oxidation of thionine dye by hydrogen peroxide in alkaline medium. The reaction has been followed spectrophotometrically by measuring the decrease in the absorbance band of thionine at 600 nm. Under the optimum conditions, the proposed method allows determination of osmium concentrations in the range of 0.1 - 220 ng ml⁻¹ with a detection limit of 0.015 ng ml⁻¹. The relative standard deviations for 11 replicate determinations of 0.20, 2.0 and 20 ng ml⁻¹ osmium (VIII) were 3.3, 1.0 and 0.69%, respectively. This method is free from most interferences, highly selective, sensitive and very stable. *Prog. Color Colorants Coat.* 3(2010), 33-40. © Institute for Color Science and Technology.

1. Introduction

The accurate determination of platinum group metals (PGM) in various matrices is one of the most difficult analytical problems. Osmium is a heavy, valuable and precious platinum metal. Nobility and catalytic activity are unique properties of osmium that result in its wide application in industry, and recently, in analysis field [1-6].

Osmium usually coexists with other platinum group metals in ores, rocks, soils, minerals and alloys. Determination of osmium in complex materials commonly includes laborious operations of sample decomposition and separation of osmium from

concomitant other elements. In order to obtain accurate values of trace osmium in these samples, it is necessary to find highly sensitive and selective method to determine this element.

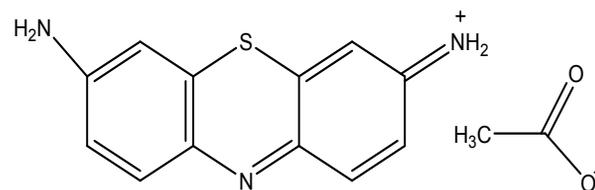
In recent years, scientists have proposed some methods for osmium determination such as electroanalytical methods [7-9], inductively coupled plasma mass spectrometry (ICPMS), inductively coupled plasma atomic emission spectrometry (ICPAES), radiochemical neutron activation analysis (RNAA) [10,11], graphite furnace atomic absorption spectrometry (GFAAS) [12], fluorescence spectrometry [13,14] and catalytic spectrophotometry [15-17].

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Some of these techniques have disadvantages, for example, by ICPMS and ICPAES, it is difficult to dissolve PGM in the procedure of sample preconcentration and the RNAA needs high radiation working environment. Catalytic kinetic analysis has many advantages such as high sensitivity, good selectivity, needing only expediency operation and simple equipment [18]. Many kinetic methods have been reported for the determination of trace amounts of osmium based on its catalytic effect on the oxidation of compounds [15-17].

A review of the recently published catalytic kinetic methods (CKM) along with the indicator reaction system, dynamic range of detection (DRD) and other general characteristics of these methods are provided in Table 1.

The poor selectivity or limit of detection, limited linear dynamic range and time consuming of many of existing methods, along with the drawback of requiring a reagent that is not commercially available compared to the proposed method, has necessitated the development of adequate separation procedures. There are a few reports on application of thionine, as an indicator reagent, for catalytic determination of some species [19-21]. The chemical formula of color thionine salt is observed in scheme 1. In the present work, we have described the application of thionine-H₂O₂ indicator reaction to the catalytic spectrophotometric determination of osmium traces. These methods have many advantages such as high sensitivity, good selectivity, required only expediency operation and simple equipment for trace determination.



Scheme 1: The chemical formula of color thionine salt.

2. Experimental

2.1. Reagents and chemicals

All chemicals used were of analytical reagents grade. Deionized water was used throughout. Osmium tetroxide stock solution was prepared by dissolving 1 g of osmium tetroxide from a sealed ampoule in about 100 ml of 0.2 M sodium hydroxide solution in a glass-stopper one liter volumetric flask. The solution was then diluted to the mark with deionized water and standardized iodometrically [22]. The working solutions were prepared by diluting the stock solution.

Hydrogen peroxide solution 0.42 M was prepared from 30% m/v hydrogen peroxide stock solution and standardized iodometrically [23]. Thionine reagent (3.48×10^{-4} M) was prepared by dissolving 0.01 g of its acetate salt in 40 ml ethanol and diluting with water to 100 ml. The buffer solutions with different pH values were prepared by mixing 0.1 M NaOH and 0.1 M H₃BO₃ (or 0.1 M citric acid with 0.2 M disodium hydrogen phosphate) in corresponding ratios. Potassium nitrate solution 2 M was prepared by dissolving its desired amount in water and diluting to 50 ml.

Stock solutions (1000 $\mu\text{g ml}^{-1}$) of interfering ions were prepared by dissolving suitable salts in water, hydrochloric acid or sodium hydroxide solution.

Table 1: A comparison of the proposed method for the determination of osmium(VIII) with the recently published catalytic kinetic methods along with the indicator reaction system, dynamic range of detection (DRD), detection limit (DL) and other general characteristics of the methods.

Indicator reaction	DRD (ng ml ⁻¹)	DL (ng ml ⁻¹)	Method comments, conditions	Ref. no
Pyrogallol red + KBrO ₃	0 - 300 300 - 1400	0.65	CKM, $\lambda_{\text{max}}=545$ nm, temp. 30 °C; time, 750 s	[15]
Gallocyanine + NaBrO ₃	0.1 - 100 100 - 1400	0.01	CKM, $\lambda_{\text{max}}=620$ nm, temp. 30 °C; time, 270 s	[16]
Carminic acid + H ₂ O ₂	0.1 - 1.5	0.02	CKM, $\lambda_{\text{max}}=540$ nm, temp. 25 °C; time, 180 s	[17]
Thionine + H ₂ O ₂	0.1 - 220	0.015	CKM, $\lambda_{\text{max}}=600$ nm, temp. 25 °C; time, 180 s	Proposed method

2.2. Apparatus

A Shimadzu model 160-A UV-VIS spectrophotometer equipped with a glass cell of 1 cm path length was used for the absorption spectra and the absorbance measurements. A Sartorius pH meter was used for pH adjustments. A thermostat (Tokyo Rikakika LTD UA-1) water bath was used to keep the temperature of all solutions at the working temperature ($25 \pm 0.1^\circ\text{C}$). A stop-watch was used for recording the reaction time.

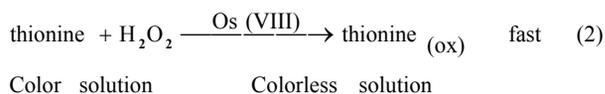
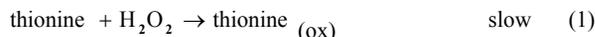
2.3. Recommended procedure

Except the catalyst concentration, which was not constant, a set of concentrations of the other reagents was judiciously chosen for analytical procedure after a detailed spectrophotometric kinetic study of the reaction. All the working solutions were thermostated at $25.0 \pm 0.1^\circ\text{C}$ for 30 min. After thermal equilibrium was established, in a 10 ml volumetric flask, 1.0 ml of buffer solution (pH = 9.0), a given volume of osmium solution and 0.3 ml of 0.42 M H_2O_2 were placed. The solution was diluted to *ca.* 8 ml with water. Then 0.7 ml of thionine was added to the reaction mixture, followed by dilution to 10 ml with water. Time was measured just after the addition of the thionine solution.

After thorough mixing, a portion of this solution was transferred to a cuvette kept in the temperature controlled cell compartment. The progress of the oxidation of thionine by H_2O_2 in alkaline medium was monitored using the "fixed time procedure" by measuring the change in absorbance at 600 nm. The data obtained were used to plot the calibration curves using difference of changes in absorbance after a fixed time ($\Delta\Delta A$) versus osmium (VIII) concentration, ($\Delta\Delta A = \Delta A_s - \Delta A_b$, ΔA_s = difference of initial absorbance and final absorbance for sample and ΔA_b = difference of initial absorbance and final absorbance for blank). This method was followed to avoid the complications, which may arise due to interference by the products or other reagents present in the system. In order to eliminate any traces of metal ions coming from glass surface, we cleaned the glassware used in this work scrupulously. Cuvettes were cleaned after use by dipping in nitric acid (1:2) for 15 min to remove traces of osmium absorbed on the walls.

3. Results and discussion

Under the conditions studied, the thionine was negligibly oxidized by hydrogen peroxide (equation 1). But the absorbance change of uncatalyzed reaction was inconsiderable (Figure 1(a)). According to equation 2, Os(VIII) at ultra trace levels can increase the rate of reaction. This oxidation process was monitored by measuring the absorbance decrease with time at 600 nm (Figure 1(b)).



3.1. Optimization of reaction variables

The reaction variables were optimized in order to maximize the sensitivity and precision of the proposed catalytic kinetic method. The effects of basicity, reagents concentration, ionic strength, temperature and time on the reaction rate were studied, where each variable was changed in turn keeping all other constant.

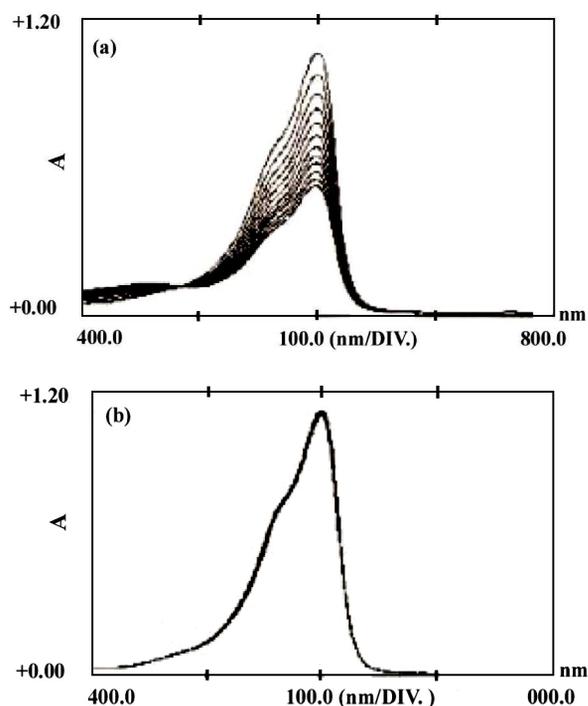


Figure 1: Absorption spectra of reaction systems (a) in the presence of osmium (VIII), and (b) in the absence of osmium. Conditions: Buffer pH = 9.0; H_2O_2 , 1.26×10^{-2} ; Thionine, 2.44×10^{-5} ; 25.0°C with scan time intervals of 15 s to 180 s.

The optimum conditions were used for the final working procedure in order to obtain best figures of merit.

3.2. Effect of pH

The effect of pH on the catalyzed and uncatalyzed reaction was studied in the pH range of 6 to 11, using three buffer solutions (ammoniacal, borate and bicarbonate) for pH adjustment. In the ammoniacal buffer medium, catalytic effect of osmium was not observed. On the other hand, in the presence of bicarbonate buffer the rate of uncatalyzed reaction was relatively high. In order to obtain the higher absorbance difference, a pH of 9.0 was fixed with a borate buffer. The variation effect of basicity on the oxidation rate of 1.74×10^{-5} M thionine in presence of 5 ng ml^{-1} osmium and 8.40×10^{-3} M H_2O_2 was studied.

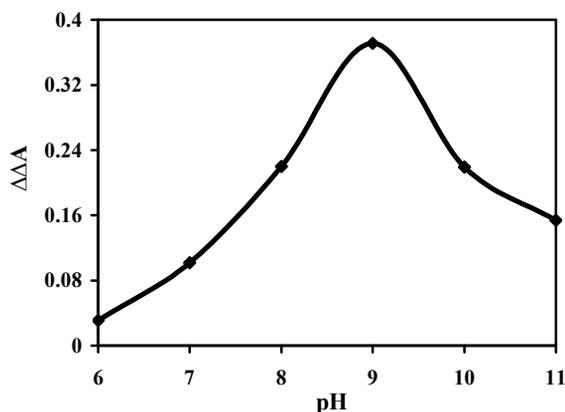


Figure 2: Effect of buffer pH. Conditions: H_2O_2 , 8.4×10^{-3} M; Thionine, 1.74×10^{-5} ; 25.0°C .

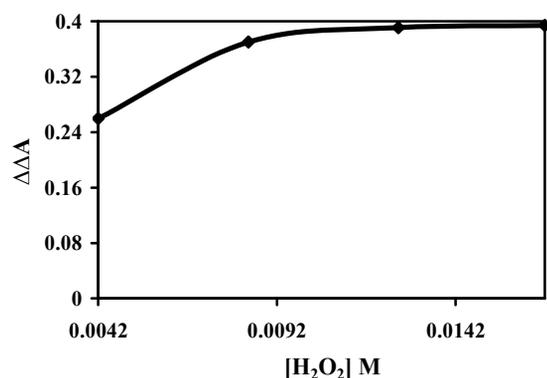


Figure 3: Effect of hydrogen peroxide concentration. Conditions: buffer pH= 9.0, Thionine, 1.74×10^{-5} ; 25.0°C .

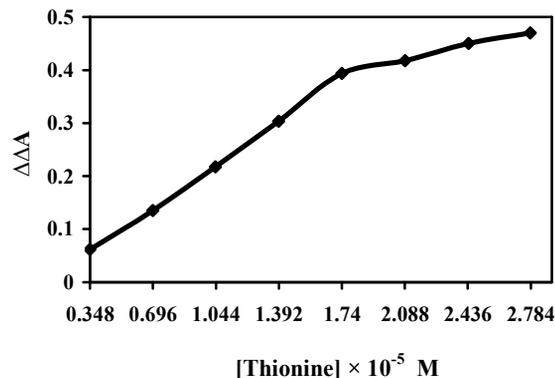


Figure 4: Effect of thionine concentration. Conditions: buffer pH= 9.0; hydrogen peroxide, 1.26×10^{-2} M, 25.0°C .

As the buffer volume (from 1 to 2.5 ml) had no effect on the difference between the absorbance changes of the catalyzed and uncatalyzed reaction, 1 ml borate buffer with pH = 9.0 was used in subsequent experiments. At pH values higher than 11, because of the formation of bubbles the reproducibility of the results was not good (Figure 2).

3.3. Effects of reagent concentrations

The effect of hydrogen peroxide concentration on the catalyzed and uncatalyzed reactions was monitored in the range of 4.20×10^{-3} to 1.68×10^{-2} M. According to the results, 1.26×10^{-2} M hydrogen peroxide was selected as the optimum working concentration (Figure 3).

Figure 4 illustrates the effect of thionine concentration on the analytical signal (sensitivity) was studied in the range of 3.48×10^{-6} to 2.78×10^{-5} M under the optimum pH and concentration of hydrogen peroxide. The rate of reaction increases linearly with thionine concentration, but the uncatalyzed reaction shows a lower increase. A limited range owing to the high molar absorptivity of the dye should be used that provides an absorbance in the range of minimum photometric error. Therefore, 2.44×10^{-5} M was chosen as the optimum concentration.

3.4. Effects of ionic strength, temperature and time

The effect of ionic strength varied from 0.02 to 0.3 M using 2 M potassium nitrate solution, on the reaction

rate was investigated. According to the results, this parameter had no effect on the reaction rate.

The effect of temperature on the reaction rate was studied in the range of 5-45 °C at the optimum reagent concentration. The results (Figure. 5) showed that 25.0 °C is the most suitable temperature, since at higher temperatures, the catalytic effect of osmium is decreased, so 25.0 °C was used throughout the study.

Optimized time was found by measuring the absorbance and its variations changing during 15-360 s after the initiation of reaction (Figure. 6). The reaction rate increases up to 180 s. At still higher time, the rate is almost constant, thus 180 s was selected as the optimum time.

3.5. Calibration and analytical parameters

Under the optimum experimental conditions mentioned above, there was a linear relationship between the difference of absorbance change of the catalyzed and uncatalyzed reactions ($\Delta\Delta A$) during a fixed time of 15-180 s and Osmium (VIII) concentration in the range of 0.1-220 ng ml⁻¹ with a correlation coefficient (*r*) of 0.9994. The regression equation was $\Delta\Delta A = 0.004 [\text{Os(VIII)}] + 0.018$. The standard deviation of the eleven independent measurements of uncatalyzed reaction rate was about 2.05×10^{-5} . The detection limit was determined to be 0.015 ng ml⁻¹ according to IUPAC definition [24]. The relative standard deviation for eleven replicate determinations of 0.2, 2 and 100 ng ml⁻¹ osmium were 3.3%, 1.0% and 0.69%, respectively. Compared with other methods mentioned in previous section, the sensitivity of this proposed method was very high (Table 2).

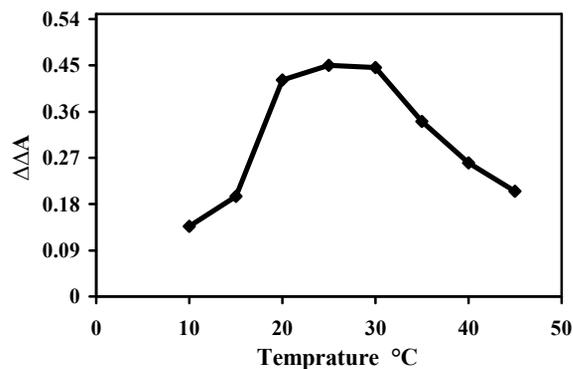


Figure 5: Effect of temperature. Conditions: buffer pH= 9.0; hydrogen peroxide, 1.26×10^{-2} M and thionine 2.44×10^{-5} M.

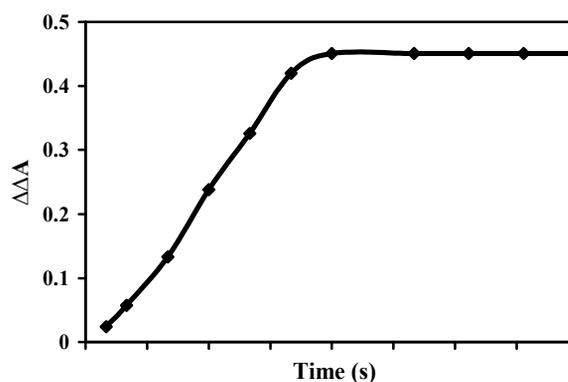


Figure 6: Effect of time reaction. Conditions: buffer pH= 9.0; hydrogen peroxide, 1.26×10^{-2} M; thionine 2.44×10^{-5} M, 25°C.

Table 2: A comparison of the precision of proposed method with the published catalytic kinetic methods.

Proposed method Os(VIII) present (ng ml ⁻¹)	Proposed method Os(VIII) found (ng ml ⁻¹)	Reported RSD% [Ref. no]			
		RSD% (n=11)	[15] (n=5)	[16] (n=8)	[17] (n=5)
0.20	0.197	3.3	-	-	4.7
0.60	0.608	2.5	-	-	3.6
1.00	0.995	1.8	-	-	2.3
2.00	2.02	1	-	1.1	-
20.00	20.01	0.69	-	0.90	-
100.0	100.0	0.42	-	-	-

Table 3: Effect of various interfering ions for the determination of 5.0 ng ml⁻¹ Os(VIII).

Interfering species	Tolerance limit (interfering species / Os(VIII))
Ca ²⁺ , Zn ²⁺ , Mg ²⁺ , Sr ²⁺ , Ba ²⁺ , Fe ²⁺ , Pt ²⁺ , SO ₄ ²⁻	
SO ₃ ²⁻ , S ₂ O ₈ ²⁻ , MoO ₄ ²⁻ , C ₂ O ₄ ²⁻ , WO ₄ ²⁻ , Na ⁺	
K ⁺ , Tl ⁺ , Ag ⁺ , SCN ⁻ , Cl ⁻ , Br ⁻ , I ⁻ , F ⁻ , NO ₃ ⁻ , NO ₂ ⁻	
HCO ₃ ⁻ , Citrate, CH ₃ CO ₂ ⁻ , Fe ³⁺ , Cr ³⁺ , La ³⁺	
Au ³⁺ , Zr ⁴⁺ , Hf ⁴⁺	3000
Se ⁴⁺ , Bi ³⁺ , Cd ²⁺ , Ni ²⁺ , Pt ⁴⁺	1000
Cu ⁺² , Al ³⁺	500
Co ²⁺ , Mn ⁺²	25

Table 4: Determination of Os(VIII) in synthetic samples under the optimum conditions.

Sample (150 ng ml ⁻¹) of each	Os(VIII) present (ng ml ⁻¹)	Mean Os (VIII) found (n=11)	RSD% (n=11)	Recovery %
Fe ⁺³ , Pd ⁺² , Cd ⁺² , Pt ⁺⁴	5.00	5.00	0.81	100
Co ⁺² , Ni ⁺² , Cu ⁺² , Mn ⁺²	5.00	4.92	0.89	98.4
Cd ⁺² , Fe ⁺² , Zr ⁺⁴ , Fe ⁺³	5.00	5.01	0.82	100.2
Pb ⁺² , Mn ⁺² , Al ⁺³ , Cu ⁺²	5.00	5.02	0.85	100.4

3.6. Interferences study

To study the selectivity of the proposed method, the influence of foreign ions on the reaction rate in the presence of Os (VIII) at optimum conditions was studied. The tolerance limit was defined as the concentration of the added ion causing not more than $\pm 4\%$ relative error for the determination of 5 ng ml⁻¹ of osmium. The results are summarized in Table 3, which clearly indicates that most common ions do not interfere with the catalytic determination. In order to remove the interfering ions, a single extraction of osmium as osmium tetraoxide into isobutyl methyl ketone (IBMK) was used, whereas other ions (or interfering ions) were not extracted. When the organic phase was shaken with 0.5 M sodium hydroxide solution, osmium tetraoxide was back-extracted into the aqueous phase.

3.7. Validity

The mixtures of common metal ions that usually accompany osmium in natural and manufactured samples were studied. In order to validate the analytical capability, i.e. to establish the reliability and

applicability of the developed method, it was applied to the determination of Os (VIII) in different synthetic samples. The results of synthetic samples are shown in Table 4. The validity of the proposed method in the analysis of samples is evident from the calculated recoveries.

4. Conclusions

The new catalytic spectrophotometric method developed for the determination of trace osmium (VIII) in synthetic samples uses readily available reagents, and is highly sensitive, selective, reproducible and inexpensive. A comparison of the proposed procedure with the various published methods is also given. This new method offers several distinct advantages such as high selectivity and sensitivity, fast and easy operation, cheaper reagents, simple and low- maintenance instruments. The reliability and simplicity of this method permit the analysis of samples with satisfactory results.

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