

**KINETICS AND ANALYTICAL APPLICATIONS OF THE  
REACTIONS BETWEEN TRIPHENYLMETHANE DYES  
AND SOME SELECTED OXIDIZING AGENTS**

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### DECLARATION BY THE CANDIDATE

I do hereby declare that the work described in this thesis was carried out by me under the supervision of Dr. (Mrs.) C.D. Jayaweera and co-supervision of Dr. P.M. Jayaweera and a report on this has not been submitted in whole or part to any university or any other institution for another Degree/Diploma .

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## TABLE OF CONTENTS

Table of contents .....	i
List of Figures.....	viii
List of Tables .....	x
Acknowledgements .....	xiii
Abstract.....	xiv
<b>CHAPTER 1: INTRODUCTION</b>	
1.1. Kinetic aspects of analytical chemistry .....	1
1.2 Triphenylmethane dyes.....	2
1.2.1 Bromopyrogallol Red .....	2
1.2.2 Previous work on BPR .....	4
1.3 Objectives of the study .....	5
1.4 Vanadium and environmental pollution .....	5
1.5 Determination of vanadium .....	6
1.6 Silver and its determination .....	7
1.7 Kinetic methods .....	10
1.8 Catalysis.....	11
1.9 Catalytic reaction.....	13
1.10 Instruments for analysis.....	14
1.10.1 Data domains .....	14
1.10.2 Analog and digital signals .....	15
1.10.3 Analog to digital converters .....	15
1.10.4 Binary counters.....	15

## CHAPTER 2: THEORY RELATED TO KINETICS

2.1 Reaction rates .....	17
2.2 Orders with respect to reactants.....	18
2.2.1 Pseudo order condition .....	18
2.3 Experimental techniques in kinetic methods of analysis.....	20
2.3.1 Conventional method.....	20
2.3.2 Mixing and timing .....	21
2.4 The kinetic theory involved in the reaction between BPR and Ce (IV) in acidic medium.....	22
2.5 The kinetic theory involved in the reaction between BPR and nitrite in acidic medium.....	24
2.5.1 The kinetic theory involved in the reaction between BPR and nitrite in acidic medium in the presence of the vanadium(IV) catalysis .....	25
2.6 The kinetic theory involved in the reaction between BPR and peroxydisulphate in acidic medium.....	27
2.6.1 The kinetic theory involved in the catalytic reaction between BPR and peroxydisulphate in acidic medium.....	29

## CHAPTER 3: EXPERIMENTAL

3.1 Kinetic study of BPR and cerium (IV) in acidic medium .....	30
3.1.1 Instrumentation.....	30
3.1.1.1 Layout of instrument .....	30

3.1.2 Chemicals and preparation of reagents for the study of the reaction between BPR and Ce(IV) .....	31
3.1.3 Methods of the study of the reaction of BPR and Ce(IV) .....	31
3.2 Kinetic study and analytical application of the reaction between BPR and nitrite in acidic medium .....	33
3.2.1 Instrumentation.....	33
3.2.2 Chemicals and preparation of reagents for kinetic study and analytical application of the reaction between BPR and nitrite in acidic medium.....	33
3.2.3 Methods for kinetic study and analytical application of the reaction between BPR and nitrite in acidic medium .....	34
3.2.3.1 Applicability of Beer's law.....	34
3.2.3.2 Study of the rate of the reaction with respect to $\text{NO}_2^-$ and $\text{H}^+$ for uncatalyzed reaction .....	35
3.2.3.3 Construction of calibration curve for determination of vanadium(IV).....	36
3.2.3.4 Study of interfering ions .....	37
3.3 Kinetic study and analytical application of the reaction between BPR and peroxydisulphate in acidic medium.....	37
3.3.1 Instrumentation.....	37
3.3.2 Chemical and preparation of reagents for kinetic study and analytical application of the reaction between BPR and peroxydisulphate in acidic medium.....	37

3.3.3 Methods for kinetic study and analytical application of the reaction between BPR and peroxydisulphate in acidic medium .....	39
3.3.3.1 Kinetic study of the uncatalyzed reaction of BPR and peroxydisulphate in acidic medium .....	39
3.3.3.2 Kinetic study of the catalyzed reaction between BPR and peroxydisulphate in acidic medium .....	41
3.3.3.3 Study of the effect of ionic strength on determination of vanadium .....	43
3.3.3.4 Kinetic study of V(IV) dependence .....	43
3.3.3.5 Study of precision and accuracy of fixed time method and slope method .....	44
3.3.3.6 Study of precision and accuracy of fixed time method .....	45
3.3.3.7 Method of preparation of total vanadium in V(V) and V(IV) mixture .....	46
3.3.3.8 Study of interfering ions .....	46
3.4 Analytical application of the reaction between bromophenol red and peroxydisulphate in acidic medium .....	49
3.4.1 Instrumentation .....	49
3.4.2 Chemical and preparation of reagents for the study of analytical application of the reaction between bromophenol red and peroxydisulphate in acidic medium .....	49
3.4.3 Methods for the study of analytical application of the reaction between bromophenol red and peroxydisulphate in acidic medium ....	50
3.4.3.1 Applicability of Beer's law .....	50

3.4.3.2 Methods to determine the optimum condition for the reaction between BPR and peroxydisulphate in acidic medium .....	51
3.4.3.3 Construction of calibration curve in the absence of 1,10-Phenanthroline.....	52
3.4.3.4 Construction of calibration curve in the presence of 1,10-Phenanthroline.....	53

## CHAPTER 4: RESULTS AND DISCUSSION

4.1 Kinetic study of the reaction between BPR and Ce (IV) in acidic medium.....	55
4.2 Kinetic study and analytical application of the reaction between BPR and nitrite in acidic medium.....	62
4.2.1 Kinetic study.....	62
4.2.1.1 Applicability of the Beer's law.....	62
4.2.1.2 Dependence of reaction rate on $\text{NO}_2^-$ for uncatalyzed reaction.....	62
4.2.1.3 Dependence of reaction rate on $\text{H}^+$ for uncatalyzed reaction .....	66
4.2.2 Calculation of overall rate constant for uncatalyzed reaction .....	66
4.2.3 Study of the catalytic action of various ions for the reaction between BPR and nitrite in acidic medium .....	69
4.2.4 Kinetic study of catalyzed reaction .....	69
4.2.5 Determination of the order with respect to vanadium(IV) and calculation of rate constant.....	73
4.2.6 Determination of the order with respect to V(IV) using another method .....	74



4.2.7 Complete rate law .....	74
4.2.8 Study of possible interferences.....	76
4.2.9 Evaluation of the accuracy of the method .....	77
4.2.10 Plausible mechanism of the reaction .....	77
4.3 Kinetic study and analytical application of the reaction between BPR and peroxydisulphate in acidic medium.....	79
4.3.1 Kinetic Study.....	79
4.3.1.1 Rate dependence on BPR .....	79
4.3.1.2 Rate dependence on peroxydisulphate .....	79
4.3.1.3 Rate dependence on hydrogen ion .....	82
4.3.1.4 Rate dependence on vanadium(IV) .....	83
4.3.1.5 Calculation of rate constant for catalytic reaction.....	84
4.3.1.6 The overall rate Law .....	85
4.3.2 Mechanism of the reaction .....	88
4.3.3 Analytical application of the reaction between BPR and peroxydisulphate in acidic medium.....	94
4.3.3.1 Effect of bromopyrogallol red .....	94
4.3.3.2 Effect of peroxydisulphate.....	95
4.3.3.3 Effect of sulphuric Acid .....	96
4.3.3.4 Effect of ionic strength .....	97
4.3.3.5 Calibration curve .....	98
4.3.3.6 Accuracy of fixed time method .....	100
4.3.3.7 Determination of total vanadium (V(V) and V(IV)) .....	100
4.3.3.8 Interference study .....	101

4.3.3.9 Analytical application.....	101
4.3.3.10 Determination of total vanadium in lagoon water sample.....	102
4.4 Analytical application of the reaction between bromophenol red and peroxydisulphate in acidic medium in the presence of silver catalyst. ....	103
4.4.1 Selection of wavelength.....	103
4.4.2 Applicability of Beer's law and selection of suitable concentration of BPRed.....	104
4.4.3 Suitable concentrations of $S_2O_8^{2-}$ and $H_3PO_4$ .....	105
4.4.4 Calibration curve .....	106
4.4.5 1,10-Phenanthroline as an activator.....	107
4.4.6 Suggestions for future work .....	109
<b>CHAPTER 5: CONCLUSION .....</b>	<b>110</b>
<b>REFERENCES .....</b>	<b>112</b>
<b>LIST OF PUBLICATIONS FROM THESIS .....</b>	<b>117</b>
<b>APPENDICES.....</b>	<b>118</b>

## LIST OF FIGURES

Figure 1.1 Structures of triphenyl methane dyes.....	3
Figure 2.1 Schematic diagram of graph of $\ln k_1$ versus $\ln [B]$ .....	20
Figure 2.2 Schematic diagram of a graph of rate versus $[BPR]$ .....	28
Figure 2.3 Schematic diagram of a graph of rate versus $[S_2O_8^{2-}]$ .....	28
Figure 3.1 Schematic diagram of a colorimeter connected to a computer ....	30
Figure 4.1 Visible spectrum of bromopyrogallol red in $0.5 \text{ mol dm}^{-3}$ acid	55
Figure 4.2 Plot of time versus $\ln$ (absorbance) for different Ce(IV) concentration .....	57
Figure 4.3 Plot of $\ln [Ce(IV)]$ versus $\ln k_1$ .....	58
Figure 4.4 Plot of time versus $\ln$ (absorbance) for different $H^+$ concentration .....	59
Figure 4.5 Plot of $\ln [H^+]$ versus $\ln k_1$ .....	60
Figure 4.6 Plot of concentration of BPR in $1 \times 10^{-3} \text{ mol dm}^{-3} H^+$ versus absorbance .....	63
Figure 4.7 Plot of time versus $\ln$ absorbance for different concentrations of $NO_2^-$ .....	64
Figure 4.8 Plot of $\ln [NO_2^-]$ versus $\ln k_1$ .....	65
Figure 4.9 Plot of time versus $\ln A$ for different $H^+$ concentration .....	67
Figure 4.10 Plot of $\ln [H^+]$ versus $\ln k_1$ .....	68
Figure 4.11 Plot of $\ln$ (absorbance) versus time for different Concentrations of V(IV).....	70
Figure 4.12 Plot of V (IV) versus rate constant $k'$ for different concentrations of V(IV).....	71

Figure 4.13 Calibration curve for vanadium(IV).....	72
Figure 4.14 Plot of $\ln [V(IV)]$ versus $\ln (k'-B)$ .....	75
Figure 4.15 Dependence of the reaction rate on BPR concentration.....	80
Figure 4.16 Dependence of the reaction rate on peroxydisulphate Concentration.....	81
Figure 4.17 Dependence of the reaction rate on hydrogen ion Concentration.....	82
Figure 4.18 Dependence of the reaction rate on vanadium concentration ....	83
Figure 4.19 Plot of $\ln [S_2O_8^{2-}]$ versus $\ln (\text{Rate})$ .....	86
Figure 4.20 Absorption curves of the reaction products .....	90
Figure 4.21 Effect of bromopyrogallol red on the reaction rate.....	94
Figure 4.22 Effect of peroxydisulphate on the reaction rate .....	95
Figure 4.23 Effect of sulphuric acid on the reaction rate .....	96
Figure 4.24 Effect of ionic strength on determination of V(IV) .....	97
Figure 4.25 Calibration curve for fixed time method.....	99
Figure 4.26 A plot of absorbance versus wavelength for bromophenol red	103
Figure 4.27 Plot of concentration of BPRed in $0.2 \text{ mol dm}^{-3} \text{ H}^+$ versus absorbance .....	104
Figure 4.28 A plot of rate versus $[S_2O_8^{2-}]$ .....	105
Figure 4.29 Calibration curve in the absence of 1,10-phenanthroline.....	107
Figure 4.30 Calibration curve in the presence of 1,10-phenanthroline .....	108

## LIST OF TABLES

Table 1.1 Dissociation constants and colour of BPR .....	4
Table 1.2 Chemical name and colour of bromophenol red .....	4
Table 1.3 Previous work on BPR with various oxidizing- agents to determine different trace constituents .....	4
Table 1.4 Some of the recent spectrophotometric methods for the determination of silver .....	10
Table 1.5 Basic components of colorimeter .....	14
Table 3.1 Volumes and concentrations of reagents taken into the cell for the determination of order with respect to Ce (IV).....	32
Table 3.2 Volumes and concentrations of reagents taken into the cell for the determination of order with respect to H <sup>+</sup> .....	32
Table 3.3 Preparative methods of solutions to check the applicability of Beer's law.....	34
Table 3.4 Volumes of reagents used to determine the order with respect to BPR and NO <sub>2</sub> <sup>-</sup> .....	35
Table 3.5 Volumes of reagents used to determine the order with respect to H <sup>+</sup> .....	36
Table 3.6 Volumes of reagents used to plot a calibration graph for the determination of V(IV).....	36
Table 3.7 Preparation of test solution for kinetic study of BPR dependence of uncatalyzed reaction .....	39
Table 3.8 Preparation of test solution for kinetic study of S <sub>2</sub> O <sub>8</sub> <sup>2-</sup> dependence of uncatalyzed reaction .....	40

Table 3.9 Preparation of test solution for kinetic study of $H^+$ dependence of uncatalyzed reaction .....	40
Table 3.10 Preparation of test solution for kinetic study of BPR dependence of catalyzed reaction .....	41
Table 3.11 Preparation of test solution for kinetic study of $S_2O_8^{2-}$ dependence of catalyzed reaction .....	42
Table 3.12 Preparation of test solution for kinetic study of $H^+$ dependence of catalyzed reaction .....	42
Table 3.13 Preparation of test solution for the determination of the effect of ionic strength .....	43
Table 3.14 Preparative method to study the V(IV) dependence.....	44
Table 3.15 Precision and Accuracy of the method.....	45
Table 3.16 Precision and Accuracy of fixed time method .....	45
Table 3.17 Preparation of test solution to determine V(IV), V(V) and total Vanadium.....	46
Table 3.18 Source of ions for interfering study.....	47
Table 3.19 Preparative method for interference study .....	48
Table 3.20 Preparative method of solution to check the applicability of Beer's law.....	50
Table 3.21 Preparation of test solution for the determination of the optimum concentration of $S_2O_8^{2-}$ solution.....	51
Table 3.22 Preparation of test solution for the determination of the optimum concentration of $H_3PO_4$ .....	52

Table 3.23 Preparative method to plot a calibration curve in the absence of 1,10- Phenanthroline.....	53
Table 3.24 Preparative method to plot a calibration curve in the presence of 1,10- Phenanthroline .....	54
Table 4.1 Cerium concentrations and rate constants at room temperature....	58
Table 4.2 Hydrogen concentrations and rate constants at room temperature	60
Table 4.3 Concentrations of $\text{NO}_2^-$ and rate constants at room temperature ..	65
Table 4.4 Concentrations of $\text{H}^+$ and rate constants at room temperature .....	68
Table 4.5 Effects of ion on the determination of V(IV) .....	76
Table 4.6 Calculated and observed rates for some selected concentrations of $\text{S}_2\text{O}_8^{2-}$ and V(IV).....	87
Table 4.7 Accuracy and precision of two methods .....	98
Table 4.8 Accuracy of results obtained by fixed time method.....	100
Table 4.9 Vanadium(IV), Vanadium(V) and Total vanadium in standard sample .....	100
Table 4.10 Effect of diverse ions on determination of $1 \mu\text{g cm}^{-3}$ V(IV) .....	101
Table 4.11 Change of rate with $\text{H}^+$ concentration .....	102
Table 4.12 Change of rate with $\text{H}^+$ concentration .....	106
Table 4.13 Accuracy of the proposed method .....	109

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**KINETICS AND ANALYTICAL APPLICATIONS OF THE REACTIONS OF  
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M.Phil. IN ANALYTICAL CHEMISTRY

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ABSTRACT

Kinetics of oxidation of Bromopyrogallol red (BPR) by cerium(IV) in sulphuric acid medium has been investigated. As this is a very fast reaction, Jenway model 6051 colorimeter was interfaced with a computer using an analog to digital converter to measure the absorbance against time. Analysis of kinetic data revealed that the reaction shows a rate law,

$$\text{Rate} = k[\text{BPR}][\text{Ce}^{4+}]^{1/2}[\text{H}^+],$$

where overall rate constant  $k = 87.95 \text{ dm}^{9/2} \text{ mol}^{-3/2} \text{ s}^{-1}$  at room temperature (30 °C).

The kinetic study of colour fading reaction between Bromopyrogallol red (BPR) and nitrite has been done in  $1 \times 10^{-2} \text{ mol dm}^{-3}$  sulphuric acid medium. The decrease in absorbance of BPR at 520 nm has been monitored colorimetrically for 5 minutes. The interference effect of various ions was also studied. The rate law was found to be,

$$\text{Rate} = k[\text{BPR}][\text{NO}_2^-][\text{H}^+]$$

and the overall rate constant was found to be  $4.32 \times 10^3 \text{ dm}^6 \text{ mol}^{-2} \text{ s}^{-1}$  at room temperature (30 °C).

A kinetic spectroscopic method for the determination of V(IV) at microgram level is described based on its catalytic activity on BPR-NO<sub>2</sub><sup>-</sup> reaction in acidic medium and a linear relation exists between the decrease in absorbance within a fixed period of time (100 seconds) in the range of 2.5 µg cm<sup>-3</sup> and 15 µg cm<sup>-3</sup>. This method is suitable for the estimation of vanadium. Based on the kinetic data it has been shown that

$$\text{Rate} = \{k_{\text{uncat}} + k_{\text{cat}} [\text{VO}^{2+}]\} [\text{BPR}] [\text{H}^+] [\text{NO}_2^-]$$

where  $k_{\text{cat}}$  was found to be  $4.42 \times 10^7 \text{ dm}^9 \text{ mol}^{-3} \text{ s}^{-1}$  and two mechanisms, one for the uncatalyzed reaction and the other for the catalyzed reaction, has been suggested.

A kinetic method is also presented for the determination of vanadium(IV) based on its catalytic effect on the redox reaction of Bromopyrogallol red (BPR) and peroxydisulphate in sulphuric acidic medium. The reaction was monitored spectrophotometrically by measuring the decrease in absorbance of BPR at 520 nm. The effect of various parameters such as concentrations of hydrogen ion, peroxydisulphate and BPR and ionic strength on the rate of the reaction was studied. Detailed kinetic studies were done. For uncatalyzed reaction the rate law obtained is

$$\text{Rate} = k_{\text{uncat}} [\text{S}_2\text{O}_8^{2-}]$$

and  $k_{\text{uncat}}$  was found to be  $3.40 \times 10^{-1} \text{ min}^{-1}$  at room temperature (30 °C). For catalyzed reaction the rate law obtained is,

$$\text{Rate} = k_{\text{uncat}} [\text{S}_2\text{O}_8^{2-}] + k_{\text{cat}} [\text{S}_2\text{O}_8^{2-}] [\text{V(IV)}]$$

and  $k_{\text{cat}}$  was found to be  $8.49 \times 10^3 \text{ dm}^3 \text{ mol}^{-1} \text{ min}^{-1}$  at room temperature (30 °C). The method is free from some interferences, which often accompany vanadium. The calibration curve obtained was linear in the range of 0.2 – 2 µg cm<sup>-3</sup>.

Preliminary investigation shows that the proposed method be used to determine vanadium(IV) and vanadium(V) in water samples. However, it is recommended that the complete study be done for the analytical applications of this method.

A kinetic spectroscopic method for the determination of  $\text{Ag}^+$  using an indicator reaction between Bromophenol red and peroxydisulphate in phosphoric acid medium with 1,10-phenanthroline has also been investigated. The detection limit of  $\text{Ag}^+$  was found to be  $27 \text{ ng cm}^{-3}$ .

The rate law of the reaction can be written as

$$\text{Rate} = \{k_{\text{uncat}} + k_{\text{cat}} [\text{Ag}^+]\} [\text{BPRed}]^a [\text{S}_2\text{O}_8^{2-}]^b [\text{H}^+]^c$$

To evaluate the accuracy of this method, solutions of known strengths of  $\text{Ag}^+$  were analyzed and the accuracy was found to be satisfactory.