

***Some Kinetic Aspects of Analytical Interest***

THESIS SUBMITTED  
BY

**ASHRAF ABDEL-AATY MOHAMED**

M.Sc. (Chemistry) 1991

TO  
CHEMISTRY DEPARTMENT  
FACULTY OF SCIENCE  
A'IN SHAMS UNIVERSITY

FOR  
DOCTOR OF PHILOSOPHY  
IN CHEMISTRY

SUPERVISED BY

Dr. M. F. El-shahat  
Prof. of Analytical and  
Organic Chemistry  
Faculty of Science  
Ain Shams University

Dr. T. Fukasawa  
Emerit. Prof. of  
Analytical Chemistry  
Faculty of Engineering  
Yamaguchi University

**1995**

### **Acknowledgment**

First and foremost, I would like to thank **God** for giving me the opportunity and will-power to accomplish this work.

I would like to express my deep gratitude and appreciation to Dr. **T. Fukasawa**, Emeritus Prof. of Analytical Chemistry, Faculty of Engineering, Yamanashi University, Japan, for his sincere guidance, fruitful discussions and criticism during this work.

Also, I would like to express my deep gratitude and appreciation to Dr. **M. F. El-shahat**, Prof. of Analytical and Inorganic Chemistry, Faculty of Science, Ain Shams University, for his kind supervision, encouragement and support throughout this work.

Sincere thanks are extended to Dr. **M. Iwatsuki**, Prof. of Analytical Chemistry, Faculty of Engineering, Yamanashi University, Japan, for providing the laboratory facilities and his kind guidance.

I would like to extend my thanks to all colleagues in the Faculty of Science, Ain Shams University and also in the Faculty of Engineering, Yamanashi University, for their kind assistance.

Sincere appreciation should be expressed to **The Ministry of Education, Egypt**, for its support during my study in Japan.

*Ashraf A. Mohamed*



**List of publications from the present dissertation:**

- 1]- "Catalytic determination of iodide using the promethazine-hydrogen peroxide redox reaction".

Mohamed, A. A., Iwatsuki, M., El-shahat, M. F. and Fukasawa, T.;

\* *Proceedings of the 43rd Annual Meeting for the Japan Society of Analytical Chemistry, Fukoka, Japan, Oct. 1994, P. 496.*

\* *Analyst*, 1995, 120, 1201.

- 2]- "Catalytic determination of vanadium using the perphenazine-bromate redox reaction and citric acid activator".

Mohamed, A. A., Iwatsuki, M., Fukasawa, T. and El-shahat, M. F.;

\* *Proceedings of the 44th Annual Meeting for the Japan Society of Analytical Chemistry, Sapporo, Japan, Sept. 1995.*

\* *Analyst*, in press.

- 3]- "Sensitive determination of trace iodide using its catalytic effect on the hydrogen peroxide oxidation of prochlorperazine".

Mohamed, A. A., El-shahat, M. F., Fukasawa, T. and Iwatsuki, M.;

\* *Proceedings of the 5th Ibn Sina International Conference on Pure and Applied Heterocyclic Chemistry, Cairo, Egypt, to be presented, Dec. 1995.*

\* *Anal. Chem. Acta*, Communicated.

- 4]- "Sensitive determination of nitrite using its catalytic effect on the bromate oxidation of prochlorperazine".

\* *Idem; Analyst*, in press.

- 5]- "Trace determination of nitrite using its catalytic effect on the perphenazine-bromate redox reaction".

\* *Idem; Anal. Sci*, Communicated.

- 6]- "Determination of trace vanadium using its catalytic effect on the prochlorperazine-bromate reaction and citric acid activator".

\* *Proceedings of the 5th Ibn Sina International Conference on Pure and Applied Heterocyclic Chemistry, Cairo, Egypt, to be presented, Dec. 1995.*

\* *Idem; Anal. Chem. Acta*, Communicated.

### List of abbreviations

<i>Abbr.</i>	<i>Referent</i>
AAS	Atomic Absorption Spectrometry
CPH	Chlorpromazine-Hydrochloride
ICP-AES	Inductively coupled plasma - Atomic emission spectrometry
ICP-MS	Inductively coupled plasma - Mass spectrometry
NAA	Neutron activation analysis
PCP	Prochlorperazine
PM	Promethazine
PP	Perphenazine
PTD	Phenothiazine derivative
PTD <sup>*</sup>	Colored radical cation of phenothiazine derivative
PTD <sup>**</sup>	Colorless sulphoxide derivative
PTFE	Polytetrafluoroethylene
THNS	2 - Hydroxy naphthaldehyde thiosemicarbazone

## **CONTENTS**

Abstract	1
List of Figures	2
List of Tables	5
Summary	7

### **PART I : INTRODUCTION**

I.1. Principles and classification of catalytic methods	10
I.2. Historical view of catalytic analysis	13
I.3. Activation and inhibition	14
I.4. Sensitivity and detection limit	15
5. Properties and analytical applications of phenothiazines	18
I.6. Methods of iodide determination	22
I.7. Methods of nitrite determination	24
I.8. Methods of vanadium determination	27

### **PART II : EXPERIMENTAL**

II.a. Apparatus	32
II.b. Reagents	32
1. General reagents	32
2. Reagents for iodide determination using the promethazine-hydrogen peroxide reaction	33
3. Reagents for iodide determination using the prchlorperazine-hydrogen peroxide reaction	34
4. Reagents for nitrite determination using the prochlorperazine-bromate reaction	34
5. Reagents for nitrite determination using the perphenazine-bromate reaction	34
6. Reagents for vanadium determination using the perphenazine-bromate reaction	34

7. Reagents for vanadium determination using the prochlorperazine-bromate reaction	35
II.C. Recommended procedures	35
1. Determination of iodide using the promethazine-hydrogen peroxide reaction	36
2. Determination of iodide using the prochlorperazine-hydrogen peroxide reaction	36
3. Determination of nitrite using the prochlorperazine-bromate reaction	37
4. Determination of nitrite using the perphenazine-bromate reaction	37
5. Determination of vanadium using the perphenazine-bromate reaction	38
6. Determination of vanadium using the prochlorperazine-bromate reaction	38

## **PART III : RESULTS AND DISCUSSION**

<b><u>Chapter 1.</u></b> Catalytic determination of iodide using the promethazine-hydrogen peroxide reaction	40
1. Effect of acidity	40
2. Effect of promethazine concentration	42
3. Effect of hydrogen peroxide concentration	42
4. Effect of ammonium sulfate concentration	48
5. Effect of temperature	48
6. Effects of foreign ions	48
7. Determination of iodate and periodate	52
8. Calibration graph and detection limit	52
9. Kinetics and reaction mechanism	55
10. Determination of iodide in river waters	56

<b><u>Chapter 2.</u></b> Sensitive determination of trace iodide using its catalytic effect on the hydrogen peroxide oxidation of prochlorperazine	59
1. Effect of prochlorperazine concentration	59
2. Effect of hydrogen peroxide concentration	59
3. Effect of acidity	63
4. Effect of ammonium sulfate concentration	63
5. Effect of temperature	68
6. Effects of foreign ions	68
7. Determination of iodate and periodate	71
8. Calibration graph and detection limit	71
9. Kinetics and reaction mechanism	73
10. Determination of iodide in natural waters	75

<b><u>Chapter 3.</u></b> Sensitive determination of nitrite using its catalytic effect on the hydrogen peroxide oxidation of prochlorperazine	78
1. Effect of prochlorperazine concentration	78
2. Effect of bromate concentration	78
3. Effect of phosphoric acid concentration	78
4. Effects of order of addition and standing time	82
5. Effect of temperature	82
6. Effects of foreign ions	82
7. Calibration graph and detection limit	85
8. Determination of nitrite in natural waters	88

<b><u>Chapter 4.</u></b> Trace determination of nitrite using its catalytic effect on the perphenazine-bromate reaction	90
1. Effect of phosphoric acid concentration	90
2. Effect of prochlorperazine concentration	90
3. Effect of bromate concentration	94
4. Effects of order of addition and standing time	94
5. Effect of temperature	94
6. Effects of foreign ions	98



7. Calibration graph and detection limit	98
8. Determination of nitrite in natural waters	101

**Chapter 5.** Catalytic determination of vanadium using

the perphenazine-bromate redox reaction	104
1. Effect of phosphoric acid concentration	104
2. Effect of perphenazine concentration	104
3. Effect of bromate concentration	107
4. Effects of citric acid and other activators	107
5. Effect of temperature	107
6. Order of addition and effects of foreign ions	112
7. Calibration graph and detection limit	114
8. Reaction mechanism and activating effects of citric acid	114
9. Determination of vanadium in natural waters	117

**Chapter 6.** Determination of trace vanadium using  
its catalytic effect on the prochlorperazine-bromate  
reaction and citric acid activator

2. Effect of phosphoric acid concentration	121
3. Effect of prochlorperazine concentration	123
4. Effect of bromate concentration	123
1. Choice of the activator	121
5. Effect of temperature	128
6. Effects of foreign ions	128
7. Calibration graph and detection limit	131
8. Reaction mechanism and activating effects of citric acid	134
9. Determination of vanadium in natural waters	136

References	138
Arabic summary	
Arabic abstract	

## ***ABSTRACT***

### **Abstract**

#### ***Some Kinetic Aspects of Analytical Interest***

Ashraf Abdel Aaty Mohamed

*Department of Chemistry, Faculty of Science,  
Ain Shams University, Abbassia, Cairo, Egypt.*

Six kinetic-spectrophotometric methods were developed for catalytic determinations of traces of pollutants in natural waters. Namely, two methods were developed for determination of each of iodide, nitrite and vanadium ions, respectively.

Iodide was determined based on its catalytic effects on the  $\text{H}_2\text{O}_2$  oxidation of promethazine (PM) and prochlorperazine (PCP). The calibration graphs are linear for up to 12.0 and 5.0  $\text{ng ml}^{-1}$  with detection limits of 0.1 and 0.03  $\text{ng ml}^{-1}$  iodide, respectively. The reaction mechanisms were inferred. The developed methods surpassed the standard  $\text{Ce(IV)-As(III)}$  reaction along with the existing methods of NAA and ICP-MS techniques, in sensitivity, selectivity and speed.

Nitrite was determined based on its catalytic effects on the bromate oxidations of PCP and perphenazine (PP). The calibration graphs were linear for up to 70 and 40  $\text{ng ml}^{-1}$  with detection limits of 0.8 and 0.5  $\text{ng ml}^{-1}$  nitrite, respectively. The methods surpassed the well established ion-chromatographic methods along with the standard method utilizing the modified Greiss reaction, in sensitivity, selectivity and speed.

Vanadium was also determined based on the bromate oxidations of PP and PCP in presence of citric acid activator. Linear calibration graphs were obtained for up to 6.5 and 5.0  $\text{ng ml}^{-1}$  with detection limits of 0.08 and 0.05  $\text{ng ml}^{-1}$  vanadium, respectively. The reaction mechanisms were suggested and the activating effects of citric acid were elucidated. The two methods surpassed the standard Fishman-Skougsstad method along with the existing methods of NAA, AAS, ICP-AES and ICP-MS techniques in sensitivity, selectivity and speed.

**Keywords:** *Kinetic-spectrophotometric techniques; Determinations of iodide, nitrite and vanadium; Reaction mechanisms; Activating effects ; Rain and polluted river waters.*

## ***LIST OF FIGURES***

**List of Figures:**

Page

1. Absorption spectra of the red oxidation product of PM.	41
2. Effect of $\text{H}_2\text{SO}_4$ concentration on the reaction rates in the $\text{I}^-$ -PM- $\text{H}_2\text{O}_2$ system.	43
3. Effect of $\text{H}_3\text{PO}_4$ concentration on the reaction rates in the $\text{I}^-$ -PM- $\text{H}_2\text{O}_2$ system.	44
4. Effect of PM concentration on the reaction rates in the $\text{I}^-$ -PM- $\text{H}_2\text{O}_2$ system.	45
5. Effect of $\text{H}_2\text{O}_2$ concentration on the reaction rates in the $\text{I}^-$ -PM- $\text{H}_2\text{O}_2$ system.	46
6. Effect of $(\text{NH}_4)_2\text{SO}_4$ concentration on the reaction rates in the $\text{I}^-$ -PM- $\text{H}_2\text{O}_2$ system.	49
7. Effect of temperature on the reaction rates in the $\text{I}^-$ -PM- $\text{H}_2\text{O}_2$ system.	50
8. Effect of standing time on the recovery of iodate and periodate using the $\text{I}^-$ -PM- $\text{H}_2\text{O}_2$ system.	53
9. Calibration graph for iodide determination using the $\text{I}^-$ -PM- $\text{H}_2\text{O}_2$ system.	54
10. Absorption spectra of the red oxidation product of PCP.	60
11. Effect of PCP concentration on the reaction rates in the $\text{I}^-$ -PCP- $\text{H}_2\text{O}_2$ system.	61
12. Effect of $\text{H}_2\text{O}_2$ concentration on the reaction rates in the $\text{I}^-$ -PCP- $\text{H}_2\text{O}_2$ system.	62
13. Effect of $\text{H}_2\text{SO}_4$ concentration on the reaction rates in the $\text{I}^-$ -PCP- $\text{H}_2\text{O}_2$ system.	64
14. Effect of $\text{H}_3\text{PO}_4$ concentration on the reaction rates in the $\text{I}^-$ -PCP- $\text{H}_2\text{O}_2$ system.	65
15. Effect of $(\text{NH}_4)_2\text{SO}_4$ concentration on the reaction rates in the $\text{I}^-$ -PCP- $\text{H}_2\text{O}_2$ system.	67
16. Effect of temperature on the reaction rates in the $\text{I}^-$ -PCP- $\text{H}_2\text{O}_2$ system.	69
17. Effect of standing time on the recovery of iodate and periodate using the $\text{I}^-$ -PCP- $\text{H}_2\text{O}_2$ system.	72

18. Calibration graph for iodide determination using the I-PCP-H <sub>2</sub> O <sub>2</sub> system.	74
19. Effect of PCP concentration on the reaction rates in the NO <sub>2</sub> <sup>-</sup> -PCP-BrO <sub>3</sub> <sup>-</sup> system.	79
20. Effect of bromate concentration on the reaction rates in the NO <sub>2</sub> <sup>-</sup> -PCP-BrO <sub>3</sub> <sup>-</sup> system.	80
21. Effect of H <sub>3</sub> PO <sub>4</sub> concentration on the reaction rates in the NO <sub>2</sub> <sup>-</sup> -PCP-BrO <sub>3</sub> <sup>-</sup> system.	81
22. Effect of standing time before bromate addition on the the NO <sub>2</sub> <sup>-</sup> -PCP-BrO <sub>3</sub> <sup>-</sup> system.	83
23. Effect of temperature on the reaction rates in the NO <sub>2</sub> <sup>-</sup> -PCP-BrO <sub>3</sub> <sup>-</sup> system.	84
24. Calibration graph for nitrite determination using the NO <sub>2</sub> <sup>-</sup> -PCP-BrO <sub>3</sub> <sup>-</sup> system.	87
25. Absorption spectra of the red oxidation product of PP.	91
26. Effect of H <sub>3</sub> PO <sub>4</sub> concentration on the reaction rates in the NO <sub>2</sub> <sup>-</sup> -PP-BrO <sub>3</sub> <sup>-</sup> system.	92
27. Effect of PP concentration on the reaction rates in the NO <sub>2</sub> <sup>-</sup> -PP-BrO <sub>3</sub> <sup>-</sup> system.	93
28. Effect of bromate concentration on the reaction rates in the NO <sub>2</sub> <sup>-</sup> -PP-BrO <sub>3</sub> <sup>-</sup> system.	95
29. Effect of standing time before bromate addition on the the NO <sub>2</sub> <sup>-</sup> -PP-BrO <sub>3</sub> <sup>-</sup> system.	96
30. Effect of temperature on the reaction rates in the NO <sub>2</sub> <sup>-</sup> -PP-BrO <sub>3</sub> <sup>-</sup> system.	97
31. Calibration graph for nitrite determination using the NO <sub>2</sub> <sup>-</sup> -PP-BrO <sub>3</sub> <sup>-</sup> system.	100
32. Effect of H <sub>3</sub> PO <sub>4</sub> concentration on the reaction rates in the V-PP-BrO <sub>3</sub> <sup>-</sup> system.	105
33. Effect of PP concentration on the reaction rates in the V-PP-BrO <sub>3</sub> <sup>-</sup> system.	106

34. Effect of bromate concentration on the reaction rates in the V-PP-BrO <sub>3</sub> <sup>-</sup> system.	108
35. Effect citric acid concentration on the reaction rates in the V-PP-BrO <sub>3</sub> <sup>-</sup> system.	110
36. Effect of temperature on the reaction rates in the V-PP-BrO <sub>3</sub> <sup>-</sup> system.	111
37. Calibration graph for vanadium determination using the V-PP-BrO <sub>3</sub> <sup>-</sup> system.	115
38. Effect citric acid concentration on the reaction rates in the V-PCP-BrO <sub>3</sub> <sup>-</sup> system.	124
39. Effect of H <sub>3</sub> PO <sub>4</sub> concentration on the reaction rates in the V-PCP-BrO <sub>3</sub> <sup>-</sup> system.	125
40. Effect of PCP concentration on the reaction rates in the V-PCP-BrO <sub>3</sub> <sup>-</sup> system.	126
41. Effect of bromate concentration on the reaction rates in the V-PCP-BrO <sub>3</sub> <sup>-</sup> system.	127
42. Effect of temperature on the reaction rates in the V-PCP-BrO <sub>3</sub> <sup>-</sup> system.	129
43. Calibration graph for vanadium determination using the V-PCP-BrO <sub>3</sub> <sup>-</sup> system.	132