การตรวจวัดเชิงสีของนิกเกิลโดยใช้แผ่นเงินระดับนาโนเมตรที่ดัดแปรด้วยกลูตาไธโอนและแอล-ซิสเตอีน

นางสาวธัญญาภรณ์ เกียรติกำจร

วิทยานิพนธ์นี้เป็นส่วนหนึ่งของการศึกษาตามหลักสูตรปริญญาวิทยาศาสตรมหาบัณฑิต
สาขาวิชาเคมี ภาควิชาเคมี
คณะวิทยาศาสตร์ จุฬาลงกรณ์มหาวิทยาลัย
ปีการศึกษา 2556
ลิขสิทธิ์ของจุฬาลงกรณ์มหาวิทยาลัย

5472826723

COLORIMETRIC DETECTION OF NICKELS USING SILVER NANOPLATES MODIFIED WITH GLUTATHIONE AND L-CYSTEINE

Miss Thanyaporn Kiatkumjorn

A Thesis Submitted in Partial Fulfillment of the Requirements
for the Degree of Master of Science Program in Chemistry
Department of Chemistry
Faculty of Science
Chulalongkorn University
Academic Year 2013

Copyright of Chulalongkorn University

Thesis Title	COLORIMETRIC DETECTION OF NICKELS USING SILVER NANOPLATES MODIFIED WITH GLUTATHIONE AND L-CYSTEINE
By	Miss Thanyaporn Kiatkumjorn
Field of Study	Chemistry
Thesis Advisor	Professor Orawon Chailapakul, Ph.D.
Thesis Co-Advisor	Assistant Professor Narong Praphairaksit, Ph.D.

Accepted by the Faculty of Science, Chulalongkorn University in Partial Fulfillment of the Requirements for the Master's Degree

.....Dean of the Faculty of Science

(Professor Supot Hannongbua, Dr.rer.nat.)

THESIS COMMITTEE

.....Chairman

(Associate Professor Vudhichai Parasuk, Ph.D.)

.....Thesis Advisor

(Professor Orawon Chailapakul, Ph.D.)

.....Thesis Co-Advisor

(Assistant Professor Narong Praphairaksit, Ph.D.)

.....Examiner

(Associate Professor Nattaya Ngamrojnavanich, Ph.D.)

.....External Examiner

(Assistant Professor Weena Siangproh, Ph.D.)

ธัญญาภรณ์ เกียรติกำจร : การตรวจวัดเชิงสีของนิกเกิลโดยใช้แผ่นเงินระดับนาโนเมตรที่ดัดแปรด้วยกลูตาไธโอนและแอล-ซิสเตอีน. (COLORIMETRIC DETECTION OF NICKELS USING SILVER NANOPLATES MODIFIED WITH GLUTATHIONE AND L-CYSTEINE) อ.ที่ปรึกษาวิทยานิพนธ์หลัก: ศ. ดร.อรวรรณ ชัยลภากุล, อ.ที่ปรึกษาวิทยานิพนธ์ร่วม: ผศ. ดร.ณรงค์ ประไพรักษ์สิทธิ์, 85 หน้า.

อุปกรณ์รับรู้เชิงสีแบบใหม่ร่วมกับอนุภาคระดับนาโนเมตรของเงินสำหรับการตรวจวัดนิกเกิลได้ถูกพัฒนาขึ้น โดยกลูตาไธโอนและซิสเตอีนถูกนำมาใช้ในการดัดแปรผิวหน้าอนุภาคระดับนาโนเมตรของเงิน ซึ่งให้การตรวจวัดที่จำเพาะกับนิกเกิลเมื่อเทียบกับโลหะอื่น ๆ ภายใต้ภาวะการตรวจวัดที่เฉพาะเจาะจง เมื่อเติมนิกเกิลในสารละลายอนุภาคระดับนาโนเมตรของเงินที่ถูกดัดแปรผิวหน้า สีของสารละลายเกิดการเปลี่ยนแปลงสามารถมองเห็นอย่างชัดเจนด้วยตาเปล่าเนื่องจากอนุภาคระดับนาโนเมตรของเงินถูกชักนำให้เกิดการรวมตัวกัน โดยเกิดการจับกันระหว่างนิกเกิลและลิแกนด์ เพื่อยืนยันการจัดเรียงตัวเองอย่างสมบูรณ์ของกลูตาไธโอนและซิสเตอีนบนผิวหน้าของอนุภาคระดับนาโนเมตรของเงิน สารละลายอนุภาคระดับนาโนเมตรของเงินที่ถูกดัดแปรนั้นถูกตรวจสอบคุณลักษณะโดยใช้เทคนิคฟูเรียร์ทรานสฟอร์มอินฟราเรดสเปกโทรสโกปี ยูวี-วิซิเบิลสเปกโทรสโกปี และกล้องจุลทรรศน์อิเล็กตรอนชนิดส่องผ่าน ตามลำดับ นอกจากนี้พารามิเตอร์ต่าง ๆ ในการตรวจเชิงปริมาณของนิกเกิล ได้แก่ อัตราส่วนของตัวดัดแปร ผลกระทบของค่าพีเอช ระยะเวลาที่ใช้ในการเกิดปฏิกิริยา และตัวรบกวนต่าง ๆ ได้ถูกตรวจสอบ จากการตรวจวัดด้วยยูวี-วิซิเบิลสเปกโทรโฟโตมิเตอร์ของนิกเกิลภายใต้สภาวะที่เหมาะสม ความสัมพันธ์เป็นเส้นตรงเชิงปริมาณได้ถูกสร้างขึ้นในช่วง 10 ถึง 150 นาโนกรัมต่อมิลลิลิตร (ค่าสัมประสิทธิ์สหสัมพันธ์เท่ากับ 0.9971) ขีดจำกัดของการตรวจวัดเท่ากับ 7.02 นาโนกรัมต่อมิลลิลิตร หรือ 120 นาโนโมลาร์ นอกจากนี้อุปกรณ์รับรู้นี้ได้ถูกนำไปประยุกต์ใช้ในการตรวจหาปริมาณนิกเกิลในตัวอย่างน้ำยาชุบทองที่ได้จากโรงงานอุตสาหกรรมเครื่องประดับซึ่งให้ผลการตรวจวัดเป็นที่น่าพอใจ ดังนั้นจึงสรุปได้ว่าวิธีทางเลือกนี้เป็นวิธีที่ง่าย รวดเร็ว ไวและมีความจำเพาะในการตรวจวัดนิกเกิล

ภาควิชา เคมี ลายมือชื่อนิสิต .....

สาขาวิชา เคมี ลายมือชื่อ อ.ที่ปรึกษาวิทยานิพนธ์หลัก .....

ปีการศึกษา 2556 ลายมือชื่อ อ.ที่ปรึกษาวิทยานิพนธ์ร่วม .....

5472826723 : MAJOR CHEMISTRY
KEYWORDS: NICKEL / COLORIMETRIC DETECTION / GLUTATHIONE / L-CYSTEINE / SILVER NANOPLATES

THANYAPORN KIATKUMJORN: COLORIMETRIC DETECTION OF NICKELS USING SILVER NANOPLATES MODIFIED WITH GLUTATHIONE AND L-CYSTEINE. ADVISOR: PROF. ORAWON CHAILAPAKUL, Ph.D., CO-ADVISOR: ASST. PROF. NARONG PRAPHAIRAKSIT, Ph.D., 85 pp.

A novel colorimetric sensor based on silver nanoplates (AgNPls) for detecting nickel ions (Ni(II)) has been developed. Glutathione (GSH) and L-cysteine (Cys) have been used to modify the AgNPls surface, exhibiting extremely high selectivity towards Ni(II) over other metal ions under specific conditions. Upon addition of Ni(II) to the modified AgNPls solution, color change can be clearly observed by naked eyes due to the aggregation of AgNPls induced by the binding between Ni(II) and the ligands. To verify a complete self-assembly of the GSH and Cys onto AgNPls suface, the modified AgNPls were characterized using fourier transform infrared spectroscopy (FTIR), ultraviolet-visible spectroscopy (UV-vis), and transmission electron microscopy (TEM), respectively. In addition, various parameters for Ni(II) quantification including modifier ratio, pH effect, incubation time, and interferences were investigated. From UV-vis spectrophotometric measurement of Ni(II) under optimal conditions, a quantitative linearity was established in the range of 10-150 ng/mL (R^2 = 0.9971) with the detection limit of 7.02 ng/mL or 120 nM (S/N=3), determine Ni(II). Furthermore, this sensor has been applied to the determination of Ni(II) in real gold plating solutions from a jewelry factory with satisfactory results. Overall, this alternative approach presents a simple, rapid, sensitive, and selective detection of Ni(II).

Department:	Chemistry	Student's Signature	Thanyaporn Kiatkumjorn
Field of Study:	Chemistry	Advisor's Signature	
Academic Year:	2013	Co-Advisor's Signature	

ACKNOWLEDGEMENTS

First of all, I am heartily grateful and sincerely appreciating to my thesis advisor, Professor Dr. Orawon Chailapakul, for her helpful advice, kind encouragement and excellent support throughout my Master's Degree study at Chulalongkorn University. I am also coordially thankful to my thesis co-advisor, Assistant Professor Dr. Narong Praphairaksit, for his kind advice and encouragement.

Furthermore, I would like to thank my thesis examination committee, Associate Professor Dr. Vudhichai Parasuk and Associate Professor Dr. Nattaya Ngamrojnavanich who gave helpful comments and suggestions in this thesis. My sincere appreciation is also extended to Assistant Professor Dr. Weena Siangproh for her excellent and helpful comments.

I especially would like to thank Associate Professor Dr. Sanong Ekgasit, Sensor Research Unit at the Department of Chemistry, Chulalongkorn University, for the synthesis of AgNPls.

An important factor in this thesis, I sincerely appreciate the Center of Excellence on Petrochemical and Materials Technology (PETROMAT) and the 90th Anniversary of Chulalongkorn University Fund (Ratchadaphiseksomphot Endowment Fund) for financial support.

Special thanks are also extended to the members of Electrochemistry and Optical Spectroscopy Research Unit, for their help, kindness and warm friendship. I also would like to thank Mr. Poomrat Rattanarat who gave constructive advices and suggestions to improve my writing skills.

Finally, my thesis, my education and my life would not have been successful without my beloved family who were always by my side and supported me in every way.

CONTENTS

Page

THAI ABSTRACT iv
ENGLISH ABSTRACT v
ACKNOWLEDGEMENTS vi
CONTENTS vii
LIST OF TABLES xi
LIST OF FIGURES xiii
ABBREVIATIONS xvi
CHAPTER I INTRODUCTION 1
1.1 Introduction 1
1.2 Objective of the research 3
1.3 Scope of the research 3
CHAPTER II THEORY AND LITERATURE SURVEY 5
2.1 Nickel 5
2.1.1 Chemistry and application of nickel 5
2.1.2 Nickel in gold plating solutions [6] 6
2.1.3 Environmental exposure 7
2.1.4 Health effect 8
2.1.5 Conventional method for nickel (Ni(II)) determination [14] 10
2.2 Colorimetric method [15, 16] 10
2.3 Nanoparticles [19, 20] 12
2.3.1 Localized surface plasmon resonance (LSPR) [25, 26] 16
2.3.2 Silver nanoparticles 18
2.3.3 Modified surface of nanoparticles (NPs) [30] 19
2.4 Ultraviolet-visible spectrophotometry [31] 21
2.5 Literature survey 26
2.5.1 Conventional methods for Ni(II) detection 26
2.5.2 Colorimetric methods for Ni(II) detection 30

Page

2.5.3 Metal nanoparticles-based colorimetric methods for Ni(II) detection..... 32
CHAPTER III EXPERIMENTAL..... 34
3.1 Modification of AgNPls with GSH and Cys..... 34
3.1.1 Instruments and equipment..... 34
3.1.2 Chemicals..... 34
3.1.3 Chemical preparation..... 35
3.1.3.1 50 mM glutathione solution (25 mL)..... 35
3.1.3.2 50 mM cysteine solution (25 mL)..... 35
3.1.4 Methodology..... 35
3.2 Characterization of GSH-Cys-AgNPls..... 36
3.2.1 Instruments and equipments..... 36
3.2.2 Methodology..... 37
3.3 GSH-Cys-AgNPls based colorimetric detection of nickel..... 37
3.3.1 Instruments and equipment..... 37
3.3.2 Chemicals..... 38
3.3.3 Chemical preparation..... 40
3.3.3.1 0.05 M phosphate buffer pH 8.0 (500 mL)..... 40
3.3.3.2 0.1 M nitric acid solution (1000 mL)..... 40
3.3.3.3 Nickel stock solution (25 mL)..... 40
3.3.3.4 Mercury stock solution (25 mL)..... 40
3.3.3.5 Arsenic stock solution (25 mL)..... 40
3.3.3.6 Cobalt stock solution (25 mL)..... 41
3.3.3.7 Zinc stock solution (25 mL)..... 41
3.3.3.8 Gold stock solution (25 mL)..... 41
3.3.3.9 Platinum stock solution (25 mL)..... 41
3.3.3.10 Rhodium stock solution (25 mL)..... 41
3.3.3.11 Silver stock solution (25 mL)..... 42

Page

3.3.3.12 Iron (III) stock solution (25 mL) 42
3.3.3.13 Iron (II) stock solution (25 mL) 42
3.3.3.14 Copper stock solution (25 mL) 42
3.3.3.15 Cadmium stock solution (25 mL) 42
3.3.3.16 Lead stock solution (25 mL) 43
3.3.3.17 Sodium stock solution (25 mL) 43
3.3.3.18 Potassium stock solution (25 mL) 43
3.3.3.19 Calcium stock solution (25 mL) 43
3.3.3.20 Magnesium stock solution (25 mL) 43
3.3.4 Methodology 44
3.4 Characterization of GSH-Cys-AgNPls aggregated with nickel 44
3.4.1 Instruments and equipments 44
3.4.2 Methodology 45
3.5 Analytical performance 46
3.5.1 Linearity 46
3.5.2 Limit of detection (LOD) 46
3.5.3 Limit of quantitation (LOQ) 46
3.5.4 Repeatability 46
3.6 The determination of nickel in real sample 47
3.6.1 Instruments and equipments 47
3.6.2 Chemicals 47
3.6.3 Sample preparation and validation of proposed method with ICP-OES . 48
CHAPTER IV RESULTS AND DISCUSSION 49
4.1 Characterization of GSH-Cys-AgNPls 49
4.2 GSH-Cys-AgNPls based colorimetric detection of nickel 51
4.3 Characterization of Ni-GSH-Cys-AgNPls aggregates 53
4.4 Optimization of the modifier ratio 54

Page

4.5 Optimization of pH 56
4.6 Optimization of incubation times 58
4.7 Selectivity of GSH-Cys-AgNPls toward Ni(II) detection 59
4.8 Analytical performance 62
4.8.1 Calibration curve 62
4.8.2 The limit of detection (LOD) and the limit of quantitation (LOQ) 64
4.8.3 Repeatability 64
4.9 Analytical application in a real sample 66
CHAPTER V CONCLUSIONS AND FUTURE PERSPECTIVE 67
5.1 Conclusions 67
5.2 Future perspective 68
REFERENCES 69
APPENDIX 77
VITA 85

LIST OF TABLES

TABLE		PAGE
2.1	The properties and general applications of AuNPs and AgNPs [24].	15
2.2	Complementary colors data [17].	22
3.1	List of instruments and equipment for the modification of AgNPls using GSH and Cys.	34
3.2	List of chemicals used for the modification of AgNPls using GSH and Cys.	34
3.3	List of instruments and equipments for the characterization of GSH-Cys-AgNPls.	36
3.4	List of instruments and equipments for the GSH-Cys-AgNPls based colorimetric detection of nickel.	37
3.5	List of Chemicals for the GSH-Cys-AgNPls based colorimetric detection of nickel.	39
3.6	List of instruments and equipments for the characterization of GSH-Cys-AgNPls aggregated with nickel.	45
3.7	List of instruments and equipments for the determination of nickel in real sample.	47
3.8	List of Chemicals for the determination of nickel in real sample.	48
4.1	Various GSH and Cys ratios on the modification of AgNPls.	54
4.2	Tolerance ratio of interfering ions in the determination of Ni(II) 70 ppb.	62
4.3	The comparison of analytical performance of different colorimetric methods using modified metal nanoparticle for the determination of Ni(II).	64
4.4	The relative standard deviations of colorimetric GSH-Cys-AgNPls sensor for detecting Ni(II) (n=11).	65

TABLE PAGE

A1 The absorbance at 618 nm of various concentration ratio of modifier onto AgNPls surface based colorimetric detection of 70 ppb Ni(II). 78

A2 The absorbance 618 nm of GSH-Cys-AgNPls based on colorimetric detection Ni(II) at different pH. 78

A3 The absorbance 618 nm of GSH-Cys-AgNPls based on colorimetric detection Ni(II) and other metals at pH 7. 79

A4 The absorbance 618 nm of GSH-Cys-AgNPls based on colorimetric detection Ni(II) and other metals at pH 8. 80

A5 The absorbance 618 nm of GSH-Cys-AgNPls based on colorimetric detection Ni(II) and other metals at pH 9. 81

A6 The absorbance 618 nm of GSH-Cys-AgNPls based on colorimetric detection Ni(II) (pH 8) at different times. 82

A7 $A_{618} - A_0$ of GSH-Cys-AgNPls based on colorimetric detection Ni(II) and other metal under optimal conditions. 83

A8 The absorbance 618 nm of GSH-Cys-AgNPls based on colorimetric detection Ni(II) in different concentration from 10 – 150 ppb. 84

A9 The absorbance at 618 nm of GSH-Cys-AgNPls and nickel level in real gold plating solutions. 84

??R470R238

LIST OF FIGURES

FIGURE PAGE

2.1 Gold-plated costume jewelry (5 μm gold-cobalt on nickel-plated tin alloy). .. 7

2.2 Jewelry allergy; (a) infected earring reaction, (b) watch strap reaction and (c) wedding ring dermatitis [10]. 8

2.3 Health effect from exposure to particulate nickel; (a) chronic bronchitis and (b) cancer of nasal cavity [11, 12]. 9

2.4 A simplified diagram of colorimeter [17]. 11

2.5 A comparative overview of the sizes of well-known items and nanoscale particles [21]. 13

2.6 Classification of nanostructured materials from the point of view of nanostructure dimensions, morphology, composition, uniformity and agglomeration state [22]. 14

2.7 A wide range in the electromagnetic spectrum obtained from various colloidal nanoparticles of different material, dimension, and shape cover. Pd: Palladium, Pt: Platinum, Ag: Silver, Au: Gold, SiOx: Silicon oxide [27]. 17

2.8 Selectivity of scattering plasmonic optical properties from various colloidal AgNPs shapes (sphere, triangle and rod, respectively). 18

2.9 Absorbance spectra of various AgNPl sizes. 19

2.10 Complementary colors 22

2.11 Components of a single-beam UV-vis spectrophotometer [32]. 23

2.12 Light sources; (a) deuterium lamp, (b) tungsten filament [33]. 23

2.13 The dispersive system; (a) diffraction grating [34], (b) prism [35]. 24

FIGURE PAGE

2.14 The photomultiplier tube consists of a photocathode, an anode, and dynodes [36]. 25

2.15 The diagram of a double-beam spectrophotometer [32]. 26

3.1 Schematic diagram for the modification of AgNPls with GSH and Cys. 36

3.2 UV-visible spectrometer HP HEWLETT PACKARD 8453 (Agilent Technologies, UK). 38

4.1 FTIR spectra of pure GSH, pure Cys and GSH-Cys modified AgNPls. 50

4.2 Absorption spectra of unmodified AgNPls and GSH-Cys modified AgNPls in aqueous solution. 51

4.3 Schematic of modification and aggregation process of AgNPls. 52

4.4 Absorption spectra of dispersed GSH-Cys-AgNPls (solid) and aggregated GSH-Cys modified AgNPls induced by the addition of Ni(II) (dash). 53

4.5 TEM images of (a) dispersed GSH-Cys-AgNPls and (b) aggregated GSH-Cys modified AgNPls induced by the addition of Ni(II). 54

4.6 Photographs of AgNPls modified by various ratios of GSH and Cys. 55

4.7 Effect of GSH and Cys ratio on the modification of AgNPls for the detection of Ni(II) using absorbance at 618 nm. 56

4.8 (A) UV–vis spectra and (B) Absorbance at 618 nm of GSH-Cys–AgNPls solutions with different pH ranging from 2.5 to 11.0 when adding Ni(II) solution. 57

4.9 pH effect on selectivity towards Ni(II) detection in the presence of other metals. 58

FIGURE PAGE

4.10 Effect of incubation time on absorbance at 618 nm of GSH-Cys-AgNPls with the presence of Ni(II). 59

4.11 (A) Photographs, (B) UV–vis spectra of GSH-Cys-AgNPls contained with various metal ions including Fe(II), Fe(III), As(III), Co(II), Cu(II), Cd(II), Pb(II), Zn(II), Hg(II), Au(III), Rh(II), Pt(II), Ag(I), Na(I), K(I), Ca(II), Mg(II). 60

4.12 The comparison of subtracted absorbance of GSH-Cys modified AgNPls in the presence of Ni(II) and other foreign metals. 61

4.13 The UV–vis spectra of GSH–Cys-AgNPls solutions with various concentrations of Ni(II) ranging from 10 to 150 ppb with incubation time: 6 min. 63

4.14 Calibration plot of the absorbance at 618 nm versus various Ni(II) concentrations including 10 ppb, 25 ppb, 50 ppb, 75 ppb, 100 ppb, 125 ppb, and 150 ppb. 63

4.15 The stability of absorption spectra at 618 nm using colorimetric GSH-Cys-AgNPls sensor for detecting Ni(II) in optimal condition (GSH : Cys = 1:5, phosphate buffer pH 8.0 ,and incubation time 6 min). 65

ABBREVIATIONS

AAS	atomic absorption spectrometry
ICP-MS	inductively coupled plasma mass spectrometry
ICP-AES	inductive coupling plasma atomic emission spectroscopy
MNPs	metal nanoparticles
AuNPs	gold nanoparticles
AgNPs	silver nanoparticles
NPs	nanoparticles
LSPR	localized surface plasmon resonance
GSH	glutathione
Cys	L-cysteine
AgNPls	silver nanoplates
WHO	World Health Organization
EPA	United States Environmental Protection Agency
Ni	nickel
Ag	silver
Au	gold
Cu	copper
UV	ultraviolet
Pd	palladium

Pt	platinum
FTIR	fourier transform infrared spectroscopy
SiOx	silicon oxide
NPls	nanoplates
SPB	surface plasmon band
SERS	surface-enhanced Raman scattering
HPLC	high performance liquid chromatography
2-HBET	2-Hydroxybenzaldehyde N-ethylthiosemi-carbazone
BiFE	bismuth film electrode
AdSV	anodic stripping voltammetry
NN	1-nitroso-2-napthol
CSPE	carbon screen-printed electrodes
DC	direct current
DMGC*	dimethylglyoxime impregnated activated carbon
GFAAS	graphite Furnace Atomic Absorption Spectrometry
EDTA	ethylenediaminetetraacetic acid
M	mega
Ω	ohm
cm	centimeter
nm	nanometer

2284708238

mm	millimeter
mL	milliliter
µL	microliter
M	molar
mM	millimolar
nM	nanomolar
µM	micromolar
kg	kilogram
mg	milligram
µg	microgram
ng	nanogram
A	absorbance
ε	molar absorptivity
L	liter
g	gram
s	second
h	hour
LOD	limit of detection
LOQ	limit of quantitation
RSD	relative standard deviation

SD	standard deviation
°C	degree Celsius
min	minute
R^2	correlation coefficient
ppb	parts per billion
ppm	parts per million
Cions	concentration of other metal ions
$C_{Ni(II)}$	concentration of nickel ions
NAC	N-acetyl-L-cysteine
NTA	nitrilotriacetic acid