ระบบเติมสารมาตรฐานภายในแบบออนไลน์อัตโนมัติสำหรับการตรวจวัดโลหะด้วยอินดักทีฟลีคัปเปิลพลาสมาออปทิคัลอิมิสชันสเปกโทรเมตรี

นายพิชชา สิงหพันธุ์

วิทยานิพนธ์นี้เป็นส่วนหนึ่งของการศึกษาตามหลักสูตรปริญญาวิทยาศาสตรมหาบัณฑิต
สาขาวิชาเคมี ภาควิชาเคมี
คณะวิทยาศาสตร์ จุฬาลงกรณ์มหาวิทยาลัย
ปีการศึกษา 2556

AUTOMATIC ON-LINE INTERNAL STANDARD ADDITION SYSTEM FOR DETERMINATION OF METALS BY INDUCTIVELY COUPLED PLASMA OPTICAL EMISSION SPECTROMETRY

Mr. Pitcha Singhaphan

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

Thesis Title	AUTOMATIC ON-LINE INTERNAL STANDARD ADDITION SYSTEM FOR DETERMINATION OF METALS BY INDUCTIVELY COUPLED PLASMA OPTICAL EMISSION SPECTROMETRY
By	Mr. Pitcha Singhaphan
Field of Study	Chemistry
Thesis Advisor	Assistant Professor Fuangfa Unob, Ph.D.
Thesis Co-Advisor	Mahitti Puanngam, 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

(Assistant Professor Fuangfa Unob, Ph.D.)

....Thesis Co-Advisor

(Mahitti Puanngam, Ph.D.)

....Examiner

(Assistant Professor Narong Praphairaksit, Ph.D.)

....External Examiner

(Assistant Professor Atitaya Siripinyanond, Ph.D.)

พิชชา สิงหพันธุ์ : ระบบเติมสารมาตรฐานภายในแบบออนไลน์อัตโนมัติสำหรับการตรวจวัดโลหะด้วยอินดักทีฟลีคัปเปิลพลาสมาออปทิคัลอิมิสชันสเปกโทรเมตรี. (AUTOMATIC ON-LINE INTERNAL STANDARD ADDITION SYSTEM FOR DETERMINATION OF METALS BY INDUCTIVELY COUPLED PLASMA OPTICAL EMISSION SPECTROMETRY) อ.ที่ปรึกษาวิทยานิพนธ์หลัก: ผศ. ดร.เฟื่องฟ้า อุ่นอบ, อ.ที่ปรึกษาวิทยานิพนธ์ร่วม: ดร.มหิทธิ เพื่อนงาม, 103 หน้า.

พัฒนาระบบอัตโนมัติแบบออนไลน์ซึ่งประกอบด้วยวาล์ว 6 ทางที่ต่อกับท่อบรรจุสารตัวอย่างและปั๊มไซรินจ์ชนิดหลอดคู่สำหรับเติมสารมาตรฐานภายในในสารตัวอย่างก่อนการตรวจวัดโลหะด้วยอินดักทีฟลีคัปเปิลพลาสมาออปทิคัลอิมิสชันสเปกโทรเมตรี (ICP-OES) สารละลายนำพาและสารมาตรฐานถูกผลักพร้อมกันด้วยปั๊มไซรินจ์ โดยสารละลายนำพาจะผลักสารตัวอย่างเพื่อผสมกับสารมาตรฐานภายในและนำส่งสารผสมเข้าสู่ ICP-OES เพื่อการตรวจวัด ใช้อัตราการไหลของสารสู่ ICP-OES 1.50 mL/min ในการวิเคราะห์สารละลายน้ำและน้ำมัน และสำหรับการวิเคราะห์น้ำมัน ใช้อัตราการไหลของแก๊สออกซิเจน 0.10 L/min เมื่อใช้อัตราการไหลดังกล่าวข้างต้นและตัวอย่างปริมาตร 4 มิลลิลิตร พบว่าจำนวนการวิเคราะห์สารตัวอย่างในน้ำและน้ำมัน คือ 11 และ 14 ตัวอย่าง ใน 1 ชั่วโมง ตามลำดับ เมื่อวิเคราะห์สารตัวอย่างโดยพิจารณาค่าการได้กลับของโลหะที่เติมลงในสารตัวอย่าง สรุปค่าได้ดังนี้ สำหรับการตรวจวัดโลหะ Cr Cu Mn และ Ni ในสารละลายน้ำ ค่าการได้กลับ คือ ร้อยละ 98.9-111.5 สำหรับช่วงความเข้มข้นต่ำกว่า 10 μg/L ร้อยละ 93.3-112.2 สำหรับช่วงความเข้มข้นระหว่าง 10-100 μg/L และร้อยละ 85.9–108.0 สำหรับช่วงความเข้มข้นที่สูงกว่า 100 μg/L และขีดต่ำสุดของการตรวจวัดอยู่ในช่วง 2.5-6.4 μg/L สำหรับการตรวจวัดโลหะ Al Cr Cu Fe Pb และ Sn ในตัวอย่างน้ำมัน ค่าการได้กลับอยู่ในช่วงร้อยละ 89.46–104.74 และขีดต่ำสุดของการตรวจวัดอยู่ในช่วง 0.22-2.71 μg/g เมื่อเปรียบเทียบผลการวิเคราะห์ระหว่างวิธีการดังกล่าวกับวิธีการนำสารตัวอย่างเข้าสู่ ICP-OES โดยตรงด้วยปั๊มเพอริสตัลติกของ ICP-OES พบว่า ค่าการได้กลับและค่าร้อยละการเบี่ยงเบนมาตรฐานสัมพัทธ์ของผลวิเคราะห์ที่ได้จากวิธีการที่นำเสนออยู่ในช่วงที่ยอมรับได้และดีกว่า ตรวจสอบความแม่นยำของวิธีการวิเคราะห์โดยพิจารณาผลการวิเคราะห์สารอ้างอิงที่ได้รับการรับรองทั้งในตัวอย่างน้ำ (ERM-CA0022a) และน้ำมัน (WM-11-NMS-5X-1) พบว่า ผลการทดลองอยู่ในช่วงที่ยอมรับได้ นอกจากวิธีการข้างต้น ระบบอัตโนมัติดังกล่าวยังสามารถนำไปประยุกต์ใช้กับการตรวจวัด Cr (VI) ร่วมกับอัลตราไวโอเลตวิสิเบิลสเปกโทรโฟโตมิเตอร์ โดยใช้อัตราการไหลที่เหมาะสม คือ 2.00 mL/min และวิธีการดังกล่าวให้ความแม่นยำในช่วงที่ยอมรับได้

ภาควิชา เคมี
สาขาวิชา เคมี
ปีการศึกษา 2556

ลายมือชื่อนิสิต ....
ลายมือชื่อ อ.ที่ปรึกษาวิทยานิพนธ์หลัก ....
ลายมือชื่อ อ.ที่ปรึกษาวิทยานิพนธ์ร่วม ....

5472050023 : MAJOR CHEMISTRY
KEYWORDS: INDUCTIVELY COUPLED PLASMA OPTICAL EMISSION SPECTROMETRY / AUTOMATIC ON-LINE SYSTEM / DETERMINATION OF METALS / INTERNAL STANDARD METHOD / ULTRAVIOLET-VISIBLE SPECTROPHOTOMETRY

PITCHA SINGHAPHAN: AUTOMATIC ON-LINE INTERNAL STANDARD ADDITION SYSTEM FOR DETERMINATION OF METALS BY INDUCTIVELY COUPLED PLASMA OPTICAL EMISSION SPECTROMETRY. ADVISOR: ASST. PROF. FUANGFA UNOB, Ph.D., CO-ADVISOR: MAHITTI PUANNGAM, Ph.D., 103 pp.

A new automatic on-line system that consisted of a 6-port valve equipped with a sample loop and a 2-channel syringe pump was developed for the addition of internal standard solution to sample solution before the determination by inductively coupled plasma optical emission spectrometry (ICP-OES). By the dual syringe pump, the carrier solution was pushed, simultaneously with the internal standard solution, to deliver the sample solution to mix with the internal standard solution. The mixture was consecutively directed to ICP-OES. The solution introduction flow rate at 1.50 mL/min was used in the determination of metals in aqueous samples and oil samples. The oxygen additional gas flow rate of 0.10 L/min was used in the analysis of oil samples. Under the suitable operating conditions using 4-mL sample volume, the sample throughput for the analysis of metals ions in aqueous solution and oil were 11 and 14 samples per hour, respectively. In the determination of Cr, Cu, Mn and Ni in spiked aqueous samples, the recoveries of metals were in the range of 98.9-111.5 % for samples having metal concentration lower than 10 μg/L level, 93.3-112.2 % for 10-100 μg/L level, and 85.9–108.0 % for the concentration higher than 100 μg/L level. The limits of detection were in the range of 2.5-6.4 μg/L. In the determination of Al, Cr, Cu, Fe, Pb, and Sn in spiked oil samples, the recoveries of metals were in the range of 89.46–104.74 %. The limits of detection were in the range of 0.22-2.71 μg/g. When the results of the sample analysis by the proposed method were compared to those from direct injection using the ICP-OES peristaltic pump, it was found that the recoveries and %RSD of the results obtained from the proposed method were in acceptable ranges and better than another method. The accuracies of the determination of metals in certified reference aqueous samples (ERM-CA022a) and certified oil samples (WM-11-NMS-5X-1) were evaluated and the proposed methods provided the results with high and acceptable accuracy. Moreover, the automatic on-line solution addition system can be applied to determine chromium (VI) by coupling the system to ultraviolet-visible spectrophotometer. The suitable solution introduction flow rate was 2.00 mL/min. The system provided an acceptable performance in the measurement of chromium (VI). This method provided the acceptable accuracies.

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

ACKNOWLEDGEMENTS

This thesis could not be completed without my advisor and co-advisor, Assistant Professor Dr. Fuangfa Unob and Dr. Mahitti Puanngam, respectively. I would like to express my appreciation for their sincere carefulness, priceless advice, and valuable suggestion during the time of thesis. Moreover, I am grateful to my thesis committee, Assocciate Professor Dr. Vudhichai Parasuk; Assistant Dr. Narong Praphairaksit; and Assistant Dr. Atitaya Siripinyanond for their valuable comments as thesis examiners.

I would like to present my gratefulness to Assistant Professor Dr. Wanlapa Aeungmaitripirom and Assistant Professor Dr. Apichat Imyim for their suggestions and helps. Next, I would like to thank all Environmental Analysis Research Unit (EARU) members and my friends, especially, Acting Sub Lt. Sira Nitiyanontakit; Miss Nattaporn Chanthasakda; and Mr. Kraisorn Hongchabok for their advice, helps, and encouragement. In addition, I would like to thank Mr. Suradej Phetkate and Miss Winatda Rodtong including her family for precious oil samples.

This research has been financially supported by SciSpec Company Limited along with the Development and Promotion of Science and Technology Talents Project (DPST).

Finally, I am grateful to my beloved family for their love and encouragement. All of usefulness of this research, I dedicate to my parents and sibling.

CONTENTS

LIST OF TABLES

Table **Page**

Table **Page**

LIST OF SCHEMES

Scheme **Page**

LIST OF FIGURES

Figure **Page**

Figure **Page**

LIST OF ABBREVIATIONS

ICP-OES = inductively coupled plasma optical emission spectroscopy

UV-Vis = ultraviolet-visible spectroscopy

K = Kelvin

nm = nanometre

g = gram

mg = milligram

µg = microgram

ng = nanogram

cSt = centiStroke

min = minute

L = litre

mL = millilitre

DPC = 1, 5-diphenylcarbazide

SDS = sodium dodecyl sulfate

mM = millimolar

%recovery = the percentage of recovery

%RSD = the percentage of relative standard deviation

SD = standard deviation

v/v = volume by volume

w/w = weight by weight

LOD = limit of detection

LOQ = limit of quantitation

CHAPTER I

INTRODUCTION

1.1 Statement of the problem

Due to the environmental concern, metals applied in human supplies and utilizations were the subject of interest since metals, even at trace level, could potentially be hazardous to human health [1-3]; the determination of metals in environmental samples becomes important in order to monitor the level of metal contamination.

Numerous techniques for the determination of metals including ultraviolet-visible spectrophotometry (UV-Vis), flame atomic absorption spectroscopy (FAAS), and inductively coupled plasma optical emission spectroscopy (ICP-OES) have been generally employed. As a matter of fact, the dissimilar prominences on each technique bring about different application depending on the amount and type of analyte in samples and sample matrix.

ICP-OES that is one of the multi-elemental analysis techniques has various analytical prominent advantages for instance low detection limit, wide linear range, precise and accurate determination, and can be used with samples of various matrices [4-7]. ICP-OES, therefore, was widely used for metal determination [5, 8]. Many drawbacks, however, in ICP-OES such as unsteady flow rate caused by peristaltic pump and instability of plasma temperature due to matrices [9] are prone to error; although, internal standard method was often brought to correct according faulty results [10, 11]. On the other hand, there are many steps in internal standard method like solution preparation leading to tedious work and prone to personal errors [11]. That is the reason why the automatic systems have been developed in current researches to eliminate errors and also reduce sample preparation time and laborious steps.

In this research, the automatic on-line solution addition system coupled to ICP-OES detection was developed for the determination of metals in aqueous and oil solution by using internal standard method. The syringe pump providing pulsation-free sample introduction and constant and stable flow would improve the signal stability. The conditions in the operation of the automatic system were optimized. This automatic system, furthermore, was applied to determine metal by coupling to ultraviolet-visible spectroscopy.

1.2 Objective of this research

The objective of this research was firstly to establish the automatic on-line internal standard addition system for determination of metals by ICP-OES, and afterwards, to apply this automatic system to determine metal ions by using UV-Vis spectrophotometer after their reaction with an appropriate reagent solution.

1.3 Scope of this research

The scope of this research includes the establishment and the application of the automatic on-line system using internal standard method and ICP-OES for the determination of metals in aqueous and oil solution. Metals in aqueous samples were chromium, copper, manganese, and nickel and those in oil samples were aluminium, chromium, copper, iron, lead, and tin. Certain parameters of the system were investigated. Finally, the automatic system was employed for the determination of metal ions with UV-Vis spectrophotometer representing other instrument.

CHAPTER II

THEORY AND LITERATURE REVIEW

2.1 Heavy metals in natural water resource

Heavy metals are one of major toxic pollutants [12], which cause health problems to human. Their effects, despite at a few low contamination levels, are harmful to human, animals, and environment [1-3] hence the environmental authorization in every country has regulations related in this crisis. In the same way in Thailand, the Ministry of Science, Technology, and Environment has legislated the ministerial orders on the maximum permitted levels of heavy metals in drinking water, ground water, wastewater discharged from industries, etc. The determination of heavy metals in aqueous environmental samples is strongly required. The wastewater discharged from industries quality standards are shown in Table 2.1.

Table 2.1 The maximum permitted levels of some heavy metals in wastewater discharged from industries [13]

Elements	Maximum permitted level (mg L^{-1})
Chromium (III)	0.75
Chromium (VI)	0.25
Copper	2.0
Manganese	5.0
Nickel	1.0

This research focused on the analysis of chromium, copper, manganese, and nickel in aqueous samples by atomic emission spectrometry that is one of the standard techniques for the determination of metal ions recommended in the regulations.

2.2 Metals in organic samples

The analysis of metals in organic sample or oil exhibits the amount of wear metals and also the amount of additive metals. An increasing amount of wear metals and a decreasing amount of additive metal indicate engine fatigue and maintenance requirement. As shown in Table 2.2, the source of metals in oils is presented.

Table 2.2 The source of metals in oils [14-17]

Sources	Metals
Bearings	Al, Ag, Ca, Cr, Cu, Fe, Ni, Pb, Sb, Sn, Ti, Zn
Gears	Ag, Cu, Fe, Mg, Ni, Sn
Greases	Al, Ba, Ca, Li, Pb, Sb, Si, Zn
Oil additives	Ba, B, Ca, Mg, Mo, Na, P, S, Si, Sn, Zn
Seals	B, Cr, Pb, Si, Sn, Zn
Shafts	Ag, Fe, Cr, Mg

The determination of metals in oils requires the sample pretreatment that turns any sample forms to solution of less viscosity or removes sample matrix. There are numerous methods for pretreatment [17] such as dilution with organic solvent, dry ashing or dry digestion, wet digestion, and oil emulsions; furthermore, there are various analytical techniques for the determination of metals in oils for instance atomic absorption spectrometry (AAS) [18], atomic emission spectrometry [19], and mass spectrometry [17, 20].

The dilution of oil sample with organic solvent and inductively coupled plasma optical emission spectroscopy (ICP-OES) were the pretreatment and the measurement technique employed in this research, respectively because the pretreatment by dilution with organic solvent is simple, fast to perform, and calibration standards are commercially available for the determination by ICP-OES. Moreover, ICP-OES can be used to analyze samples with different matrices, which oils are included.

2.3 Analytical techniques for metal determination

2.3.1 Inductively coupled plasma optical emission spectroscopy (ICP-OES)

ICP-OES is a technique, which can be used to perform quantitative and qualitative analysis of samples [4-7, 20]. The plasma, with temperature of 7,000 to 8,000 K, can atomize almost all elements thus the technique becomes the dominant spectroscopic multi-elemental analysis [20]. The main characteristics of ICP-OES are low detection limit, wide linear range, precise and accurate determination, and it can be employed to analyze samples with various matrices such as aqueous solution and organic solution [4, 7]. The basic operation of this instrument is the introduction of nebulized solution into the center of the plasma that leads to the sample desolvation, vaporization, atomization or ionization, and excitation of gaseous atoms/ions, respectively. The excited species emit specific wavelength radiation that is detected by the detector, to return to their ground state.

On the other hand, ICP-OES also has some weakness including the error from analyst such as standard solution and sample preparation, and instrument error [9]. Hence, internal standard calibration is often used to correct those errors [10].

Internal standard [10] method is a known method to be used in the quantitative analysis of sample to overcome the error attributed from instrument condition drift during the analysis and the sample loss during the sample preparation step. Certain parameters that could uncontrollably change and affect the signal of analytes include introduction flow rate of ICP-OES peristaltic pump and the detector response. Internal standard, the substances that have same behavior as that of analytes but does not appear in the sample solutions, is added to the sample and standard solutions. The ratio of response from analyte to internal standard is employed instead of the sole the responses from analyte in the calibration curve construction and sample determination to provide higher accuracy of the analysis.

However, to use internal standard method, a same amount of internal standard must be added to standard and sample solutions, which is laborious and can cause the error [11] if the addition is performed manually. The automatic on-line system for internal standard addition is proposed in this research.

2.3.2 Ultraviolet-visible spectroscopy (UV-Vis)

UV-Vis spectroscopy is a common technique for measurement of the ultraviolet or visible radiation absorbing molecules. The advantages of the technique are high sensitivity, non-destruction of sample solution, and low operating cost [20] besides UV-Vis spectroscopy is also used as detector in other analytical instrument e.g. high performance liquid chromatography [20].

In this research, UV-Vis spectroscopy was used to determine hexavalent chromium (Cr (VI)) that reacts with 1,5-diphenylcarbazide (DPC) to give Cr (III) and oxidizing form of DPC or diphenylcarbazone. The complex of Cr (III) and diphenylcarbazone can absorb visible radiation at 540 nm. The reaction is shown as follow [21].

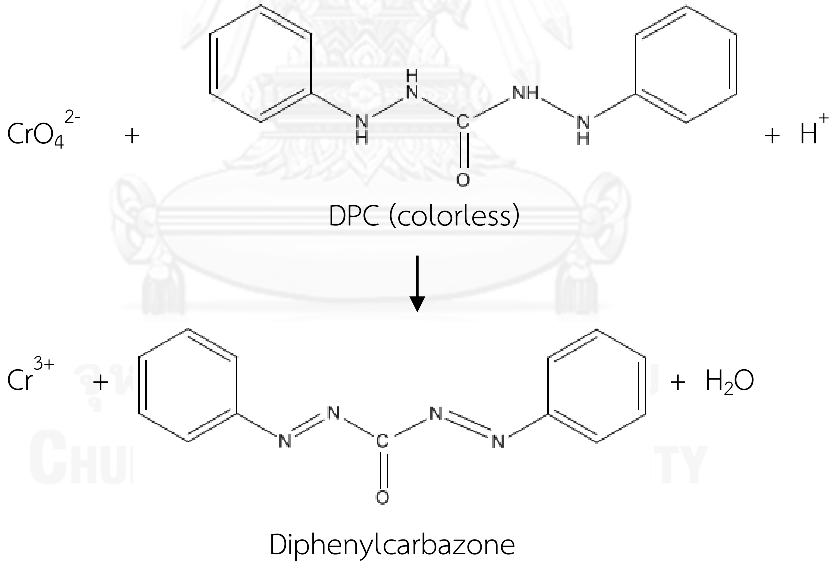


Figure 2.1 The reaction of Cr (VI) and DPC [21].

After DPC was oxidized by Cr (VI), the pink color solution from diphenylcarbazone-chromium (III) (Figure 2.2) complex will appear [21]. In general, DPC solution can be prepared in organic solvent however this research aimed to reduce the use of organic solvent thus DPC was dissolved in sodium dodecyl sulfate solution instead [22].

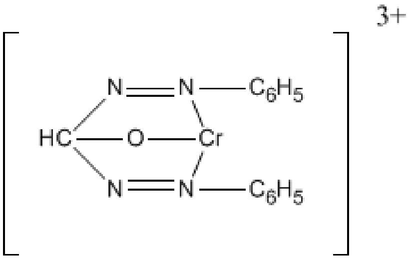


Figure 2.2 Diphenylcarbazone-chromium (III) complex [21].

2.4 Automatic on-line system

The automatic on-line solution addition system prior to the determination by spectrometric techniques such as flame atomic absorption spectroscopy (FAAS), inductively coupled plasma optical emission spectroscopy (ICP-OES), and ultravilolet-visible spectroscopy (UV-Vis) could reduce labour intensive and eliminate the sample contamination or losses of analytes, therefore the automatic systems were invented. Generally, the automatic system is often connected to an analytical instrument in order to continuously flow the solution for the determination. The examples of research that proposed the application of automatic system are described in detail below.

Themelis *et al.* [23] developed sequential injection analysis system for cyanide detection. This system consisted of multi-position valve where a sample was delivered to react with ninhydrin in carbonate solution. It gave a colorimetric gaseous complex that was further passed to a spectroscopic detector. The results showed that it could be used to analyze cyanide in drinking and tap water at the allowed level following the policies of US Environmental Protection Agency.

Tu *et al.* [24] used the automated flow injection analysis for determination of Pd and Cr ions in pharmaceutical product by inductively coupled plasma mass spectrometry (ICP-MS). This system employed online solid phase extraction for preconcentration of analytes and it could be used with a small volume sample.

Moreover, automated flow injection analysis for on-line preconcentration and determination of other metals was reported. Beck *et al.* [25] used metal chelating resin column for preconcentration of Cd, Cu, Ni, Zn, and Mn ions in estuarine water at San Francisco Bay and ICP-MS for determination. After sample was passed through the resin column under automatic system operation, metals ions adsorbed onto the column were eluted by acid solution and mixed with Rh as internal standard solution for further determination by ICP-MS.

In addition, analyte speciation with automatic system could also be performed. Jitmanee *et al.* [26] experimented Se speciation by separating selenite (H_2SeO_3) and selenate ($HSeO_4^-$) from drinking and tap water with anion exchange resin columns. The sample was delivered through the first anion exchange resin column, where selenate were adsorbed, then the rest of sample flowed to the mixing coil to react with basic solution that turned selenite to its anion form that could be extracted in the next anion exchange resin column. Se species were eluted by acidic solution and determined by ICP-MS.

The flow injection analysis systems for aqueous sample were reported; as well the systems for organic samples were developed.

Rocha *et al.* [27] developed the automatic system for investigation the amount of organic phosphorus in oils by ICP-MS. A column was used in the system for phosphorus retention and methanol as eluent.

Pinto *et al.* [28] developed sequential injection analysis system for Fe (III) analysis in oils. This system consisted of an injection valve that assisted the sample and thiocynate mixing in a chamber. The colored mixture was then analyzed by UV-Vis spectrometer.

However, the important problem for the analysis is instrument error and personal error from manual sample preparation. The internal standard was used to correct such errors; nevertheless, the methods led to tedious steps. Therefore, the automatic system designed for both the internal standard addition in standard and sample solution step and the solution determination step is beneficial.

In this research, an automatic system consisting of a 2-channel syringe pump, a peristaltic pump, and a 6-port valve is employed for both internal standard addition step and the mixed solution introduction to ICP-OES for the analysis.

CHAPTER III

EXPERIMENTAL

3.1 Analytical instruments

All analytical instruments used in this research are listed in Table 3.1.

Table 3.1 Instrument list

Instruments	Model, Manufacture
Inductively coupled plasma optical emission spectrometry (ICP-OES)	iCAP 6500, Thermo Scientific
Fiber optic ultraviolet-visible spectrometer with z-flow cell (UV-Vis)	Avaspec-2048, Avantes BV
Light source for fiber optic ultraviolet-visible spectrometer	AvaLight-DHc, Avantes BV
Syringe pump	V6-55022, Klohen
6-port Valve	VICI
Peristaltic pump	ISM827, Ismatec
Ultrasonic sonicator	UC-80, Sturdy

3.2 Chemicals

The reagents and solvents used in this research are listed in Table 3.2.

Table 3.2 Chemicals list

Chemicals	**Supplier**
Multi-element standard solution (100 mg L^{-1})	Perkin Elmer
Yttrium standard solution (1000 mg L^{-1})	Merck
Zinc standard solution (1000 mg L^{-1})	Fluka Analytical
Aluminium oil standard solution (1000 µg g^{-1}, 20 cSt)	Conostan
Chromium oil standard solution (1000 µg g^{-1}, 20 cSt)	Conostan
Copper oil standard solution (1000 µg g^{-1}, 20 cSt)	Conostan
Iron oil standard solution (1000 µg g^{-1}, 20 cSt)	Conostan
Lead oil standard solution (1000 µg g^{-1}, 20 cSt)	Conostan
Tin oil standard solution (1000 µg g^{-1}, 20 cSt)	Conostan
Yttrium oil standard solution (1000 µg g^{-1}, 20 cSt)	Conostan
Blank oil solution (20 cSt)	Conostan
PremiSolv^{TM} ICP solvent	Conostan
Potassium dichromate	Merck
1, 5-diphenylcarbazide (DPC)	Sigma-Aldrich

Table 3.2 Chemicals list (cont.)

Chemicals	**Supplier**
Sodium dodecyl sulfate (SDS)	Sigma-Aldrich
Nitric acid (65% w/w)	Merck
Sulfuric acid (95-97% w/w)	Merck
Certified reference materials:	
- Soft drinking water UK – metals	European Reference Materials
- Wear metal multi-elemental oil standard solution (50 µg g^{-1})	AccuStandard

3.3 Preparation of chemicals and reagents

3.3.1 Metals ions in aqueous solutions

Multi-element (chromium, copper, manganese, and nickel) solution, yttrium solution, and zinc solution of the desired concentrations were daily prepared by appropriate dilution of stock standard solution with 3% v/v nitric acid in Milli-Q water.

3.3.2 Metals ions in oil solutions

Multi-element (aluminium, chromium, copper, iron, lead, and tin) solutions and yttrium solution of the desired concentrations were daily prepared by dilution of appropriate amount of each metal stock oil standard solution with blank oil solution and mixing with PremiSolv^{TM}. A ratio between the amount of metal stock oil standard solution mixed with blank oil solution and the amount of PremiSolv^{TM} must be kept constant at every concentration (10% w/w of oil). After prepared, the solutions were mixed with the help of an ultrasonic sonicator.

3.3.3 Blank solution for oil sample analysis

Blank solution was daily prepared by mixing blank oil solution in PremiSolv^{TM} with the same ratio of oil in organic solvent as that used in oil samples.

3.3.4 Chromium (VI) ion stock solution

1,000 mg L^{-1} chromium (VI) ion stock solution was prepared by dissolving the appropriate amount of potassium dichromate with 3% v/v nitric acid in Milli-Q water. This stock solution was used to prepare chromium (VI) ion solutions of desired concentrations by appropriate dilution with 3% v/v nitric acid in Milli-Q water.

3.3.5 1, 5-Diphenylcarbazide solution (DPC)

6 mM DPC solution was daily prepared by dissolving the appropriate amount of DPC with 20 mM SDS solution in 2% v/v sulfuric acid in Milli-Q water with the help of an ultrasonic sonicator.

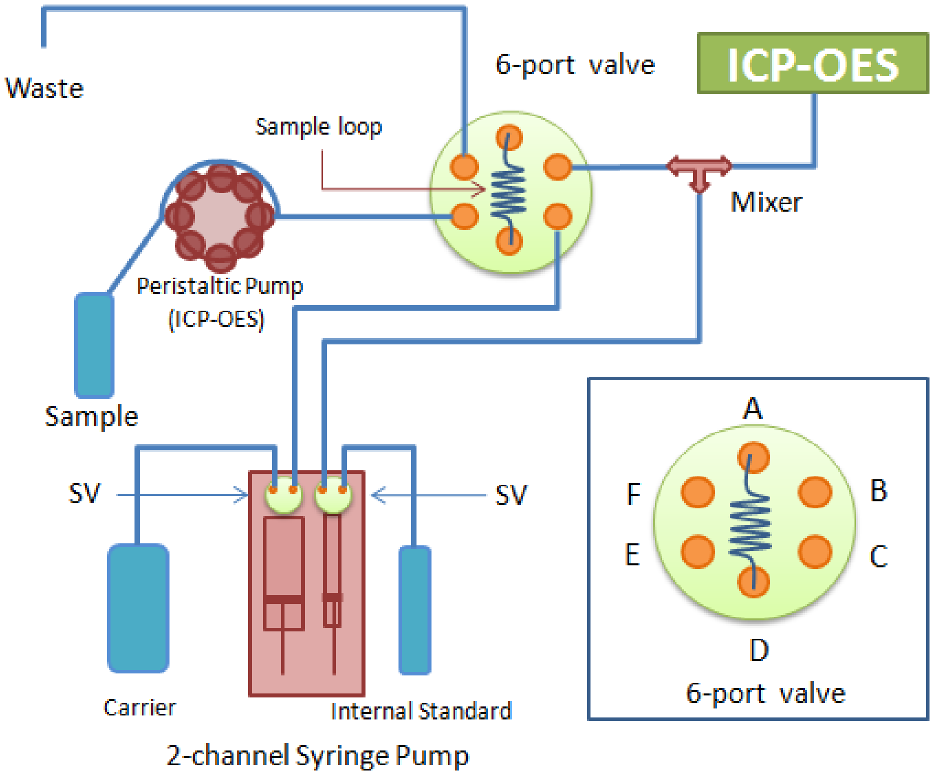
3.3.6 Sodium dodecyl sulfate solution (SDS)

20 mM SDS solution was daily prepared by dissolving the appropriate amount of SDS with 2% v/v sulfuric acid in Milli-Q water.

3.4 Determination of metals in aqueous solutions

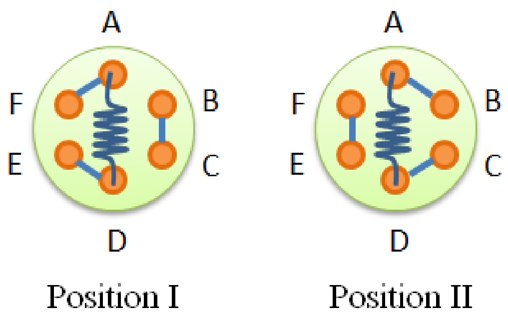
3.4.1 Automatic system setup

A schematic diagram of the automatic on-line internal standard addition system is depicted in Scheme 3.1. The system consisted of a 2-channel syringe pump equipped with syringes containing internal standard and carrier solution, a 6-port valve with 4-mL sample loop made of PTFE tube (1/8” o.d., 1.52 mm i.d.) and a peristaltic pump of ICP-OES.



Scheme 3.1 Automatic on-line internal standard addition system (SV = solenoid valve).

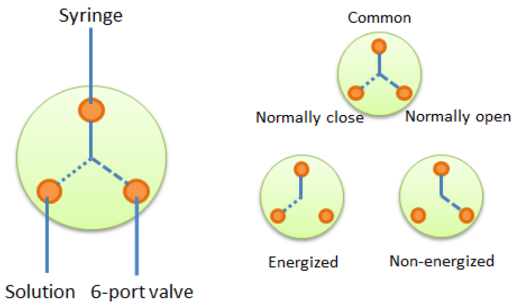
The 6-port valve could be switched to connect different ports in 2 positions as illustrated in Scheme 3.2. In position I, port A and F, port B and C, and port D and E were connected together. When the 6-port valve was programmed to switch to position II, port A and B, port C and D, and port E and F were connected instead.



Scheme 3.2 2-type position of 6-port valve.

The operation of the automatic system consisted of 2 steps: loading step and injection step. The 2-channel syringe pump was operated together with two 3-way solenoid valves to either load or inject the carrier solution (3% v/v nitric acid in Milli-Q water) and internal standard solution. The switching of the solenoid valves was performed by applying the current. Both steps in on-line internal standard addition are described below.

1. Loading step: This step was to load the sample into sample loop, meanwhile solutions into syringes. The 2-channel syringe pump was programmed to load the internal standard solution and carrier solution into the syringes; the 3-way solenoid valves were energized and switched to allow the solution to fill the syringes (Scheme 3.3). In the meantime, the sample was loaded into sample loop; the position of the 6-port valve was programmed to be in position I. Hence the sample solution was delivered into the sample loop tube through port E by the ICP-OES peristaltic pump.



Scheme 3.3 The operation of solenoid valve.

2. Injection step: The syringe pump pushed the carrier solution to flush the sample in the sample loop to mix with internal standard solution and consecutively to be detected by ICP-OES.

After cutting off the energy provided to the solenoid valves, the 6-port valve was switched to position II and the solutions in dual syringes were concurrently pushed. The carrier solution from 5.00-mL syringe was delivered through a 3-way solenoid valve to port C to flush the sample solution toward the mixer. For the addition of the internal standard solution, the internal standard solution in 100-µL syringe (zero dead volume) was pushed directly to a mixer through another 3-way solenoid valve to simultaneously mix with the sample solution. The mixture was consecutively passed to ICP-OES.

All tubes described in the system were PTFE tubes (1/8” o.d., 1.52 mm i.d.) except the tubes connected to the mixer and the carrier and internal standard solutions loading tubes were smaller diameter PTFE tubes (1/16” o.d., 0.5 mm i.d.).

3.4.2 Selection of analytical wavelength

The analytical wavelength used in this system was chosen by considering that the signal detected at that analytical wavelength should belong to only the specified elements without any response from other interfering elements.

3.4.3 Effect of solution introduction flow rate

The effect of solution introduction flow rate is an only parameter to be investigated in order to obtain high sensitivity of detection signal. The flow rate at 1.00, 1.50, and 2.00 mL min^{-1} was examined. By the previously explained procedure, the experiments were performed in triplicate. The multi-element solutions with concentration of 0.10 and 1.00 mg L^{-1} were experimented and the background signal from blank solution was also collected.

The time scan signal and average signal were recorded for all experiments. The collection of data in time scan mode was conducted in order to observe the progress of overall time-based signal while the average signal value was obtained from the results of the time scan mode in order to collect the signal value as reported in normal operation of ICP-OES.

3.4.4 Method validation

Under the optimized condition, the calibration curve was obtained by the analysis of multi-element solutions in the range of 2.0 to 10,000 µg L^{-1} by ICP-OES with the automatic system. The standard curves were constructed after repeated analysis of standards solutions 3 times within a day and 5 times within 10 days. The precision of the calibration method was exhibited as the percentage of the relative standard deviation (%RSD) of slope of linear equation from calibration curve. The limit of detection (LOD) and the limit of quantitation (LOQ) were calculated from the three times and ten times of the standard deviation (SD) of 10 measurements of blank solution containing 3% v/v nitric acid and Y solution by ICP-OES with the automatic system.

3.4.5 Analysis of water samples

The proposed method was applied to determine chromium, copper, manganese, and nickel in water samples and samples spiked with multi-element standard solution. The 12-level concentrations were 3.0, 5.0, 9.0, 30.0, 50.0, and 90.0 300.0, 500.0, 900.0, 3,000.0, 5,000.0 and 9,000.0 μg L^{-1}. All analysis of standards, samples and spiked samples were performed under the optimized condition. All samples (i.e. drinking water, pool water, tap water, river water, and wastewater) were immediately preserved with nitric acid in PET bottle after collection and twice filtered through filter paper (Whatman, No.1) before analysis. The experiment was performed in triplicate. The accuracy and precision of the method was exhibited as the percentage of recovery (%recovery) and %RSD, respectively. Furthermore, the results obtained via the automatic system were also used in the determination of metals by external standard method.

3.4.6 Analysis of certified reference material

The accuracy of the proposed method was evaluated by determining chromium, copper, manganese, and nickel contained in certified reference material (ERM-CA022a, European Reference Materials, Union of Europe) with the proposed method, compared to the certified values. The experiment was performed in triplicate.

3.5 Determination of metals in oil solutions

3.5.1 Automatic system setup

The automatic system for determination of metal in oil solution was the same setup as the system for aqueous solution analysis (see in 3.4.1). However, to suitably adapt the system for the analysis of organic solution, the tube used to load solution into sample loop was made from Viton polymer and the carrier solution was Premisolv^{TM}.

3.5.2 Selection of analytical wavelength

The selection of analytical wavelength was done with the same consideration as described in 3.4.2.

3.5.3 Effect of oxygen additional gas flow rate

The effect of oxygen additional gas flow rate was investigated in order to achieve high sensitivity of the detection; oxygen gas was added in the auxiliary argon gas to yield complete combustion of organic substances in solution and to eliminate carbon emission which could absorb and shield analyte signal by deposition on the ICP-OES torch. This parameter was examined in the oxygen flow rate at 0.05, 0.10, and 0.15 L min^{-1}. With the solution introduction flow rate at 1.50 mL min^{-1}, the experiments were performed in triplicate. The multi-element oil solutions with concentrations of 1.00 and 5.00 µg g^{-1} were selected as samples and the background signal from blank solution analysis was also collected. The time scan signal and average signal were recorded for all experiments.

3.5.4 Effect of solution introduction flow rate

The solution introduction flow rate is a parameter to be optimized in order to obtain high sensitivity of detection signal. Using the optimized oxygen additional gas flow rate, this parameter was varied from 1.00 to 2.00 mL min^{-1}. By the previously explained procedure, the experiments were done in triplicate. The multi-element oil solutions with concentration of 1.00 and 5.00 µg g^{-1} were experimented as samples and the background signal from blank solution analysis was also collected. The time scan signal and average signal were recorded for all experiments.

3.5.5 Method validation

Under the optimized condition, the calibration curve was obtained by the analysis of 0, 0.50, 2.00, 4.00, 6.00, 8.00, and 10.00 µg g^{-1} multi-element oil solutions by ICP-OES with the automatic system. The determination of standard solutions and calibration curve construction were repeated 3 times within a day and 5 times within 10 days. The precision of the calibration method was exhibited as %RSD of slope of linear equation from the calibration curve. LOD and LOQ were calculated from the three times and ten times of the standard deviation (SD) of 10 measurements of blank solution containing 10% w/w blank oil in Premisolv^{TM} and Y solution by ICP-OES with the automatic system.

3.5.6 Analysis of oil samples

The proposed method was applied to determine aluminium, chromium, copper, iron, lead, and tin in crane engine used oil and car engine used oil spiked with multi-element standard solution at 3.00 µg g^{-1} final concentration. Performed under the optimized condition, the calibration curve was obtained by injection of 0, 2.00, 4.00, 6.00, 8.00 and 10.00 µg g^{-1} multi-element oil standard solutions to ICP-OES via the automatic system and then the sample solutions were determined. The experiments were performed in triplicate. The accuracy and precision of the method was exhibited as %recovery and %RSD, respectively. The results obtained via the automatic system were also used to determine metals by external standard method Furthermore, the results obtained from internal standard method using the proposed system were compared to those collected from the direct injection of solutions prepared by manually mixing of oil standards or samples with yttrium.

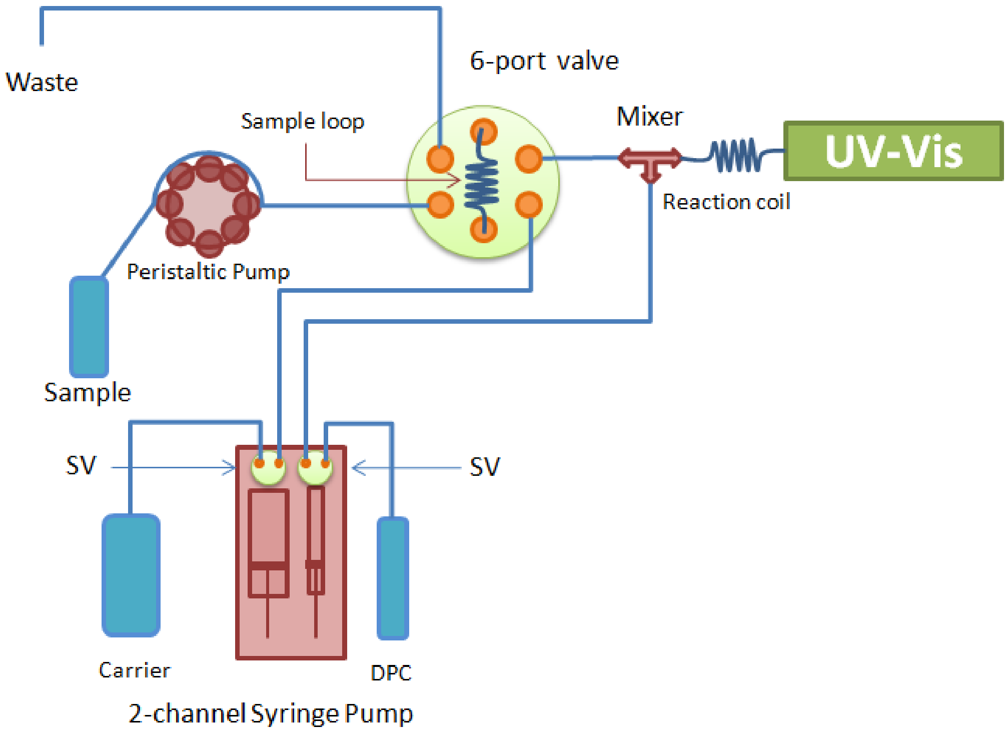
3.5.7 Analysis of certified reference material

The accuracy of the proposed method was evaluated by analyzing aluminium, chromium, copper, iron, lead, and tin contained in certified reference material (WM-11-NMS-5X-1, AccuStandard), compared to the certified value. The experiments were performed in triplicate

3.6 Determination of chromium (VI) in aqueous solution by UV-Vis spectroscopy

3.6.1 Automatic system setup

The automatic on-line analysis of chromium (VI) by UV-Vis spectroscopy was proposed using the reaction of chromium (VI) with DPC. This system was composed of a 2-channel syringe pump equipped with two 3-way solenoid valves used for solutions introduction and a 6-port valve with a 200-μL sample loop on valve. A schematic diagram of this system is shown follow.



Scheme 3.4 Automatic on-line analysis system with UV-Vis spectrophotometer (SV = solenoid valve and DPC = 1, 5-diphenylcarbazide).

The operation of this automatic system consists of 2 steps: loading step and injection step (see operating detail in 3.4.1).

1. **Loading step**: The 2-channel syringe pump was programmed to load DCP solution and carrier solution (2% v/v sulfuric acid in Milli-Q water) to fill the syringes; in the meantime, the sample was loaded into sample loop through the peristaltic pump operation via the tube made from Tygon polymer.

2. **Injection step:** The syringe pump pushed the carrier solution to flush the sample in the sample loop to subsequently mix with DPC solution in the reaction coil (200 µL) and detected in UV-Vis spectrophotometer at 540 nm consecutively.

This system was operated in the same fashion as the automatic on-line internal standard addition system for determination by ICP-OES; nevertheless, the sample loop made from PTFE tube (1/16” o.d., 0.5 mm i.d.) had a volume of 200 µL. All tubes described in the operation were made from PTFE tube (1/16” o.d., 0.5 mm i.d.). The syringes for carrier and DPC solution had a volume of 1.00 mL and 250 µL, respectively.

3.6.2 Effect of solution introduction flow rate

The effect of solution introduction flow rate is an only parameter to be optimized in order to obtain high sensitivity of detection signal. This effect was observed at the flow rate of 1.00, 1.50, and 2.00 mL min^{-1}. By the explained procedure, the experiments were done in triplicate. The standard chromium (VI) solutions of 2 concentrations: 0.50 and 1.00 mg L^{-1} were selected as the sample and the blank solution signal was also collected.

3.6.3 Method validation

Under the optimized condition, the method validation was performed by analyzing standard chromium (VI) solution at 3 concentration levels: 0.50, 1.00 and 1.40 mg L^{-1} as the synthetic sample solutions. The analysis was repeated three times for each concentration level. The calibration curved was obtained by direct injection of 0, 0.40, 0.80, 1.20, 1.60, 2.00 and 2.40 mg L^{-1} standard chromium (VI) solutions to UV-Vis spectrophotometer via the automatic system and then the sample solutions were determined. The accuracy and the precision of the method was exhibited as the percentage of recovery and %RSD, respectively. LOD and LOQ were respectively calculated from the three times and ten times of the standard deviation of 10 measurements of blank solution containing 2% v/v sulfuric acid and DPC solution by UV-Vis spectrophotometer via the automatic system.

3.6.4 Analysis of blind samples

The proposed method was applied to determine chromium (VI) in blind samples, which are the synthetic unknown samples for analyst, under the optimized condition. The calibration curved was constructed from the results of injection of 0, 0.40, 0.80, 1.20, 1.60, 2.00 and 2.40 mg L^{-1} standard chromium (VI) solutions to UV-Vis spectrophotometer via the automatic system and then the sample solutions were determined. The experiment was performed in triplicate for each sample. The accuracy and the precision of the analysis were exhibited as the percentage of recovery and %RSD, respectively.

CHAPTER IV
RESULTS AND DISCUSSION

4.1 Determination of metals in aqueous solutions

In the proposed system, the 2-channel syringe pump consisted of a 5-mL syringe and a 100-µL syringe that contained carrier and internal standard solution, respectively. By the same flow rate, the 2 syringes were pushed to simultaneously deliver the solutions to finally mix together in the mixer; therefore, the total volume of the mixture, after the solution in syringes were all delivered, was 5,100 µL. In the determination of metals in aqueous solution, the internal standard solution was a 5.10 mg L^{-1} yttrium solution and therefore the final concentration of yttrium mixed in the metal sample or standard solution was 100 µg L^{-1}.

4.1.1 Automatic system setup

Automatic system coupled to ICP-OES is shown in scheme 4.1 and the operating conditions are listed in Table 4.1 (see the photographs of the system in Appendix 1).

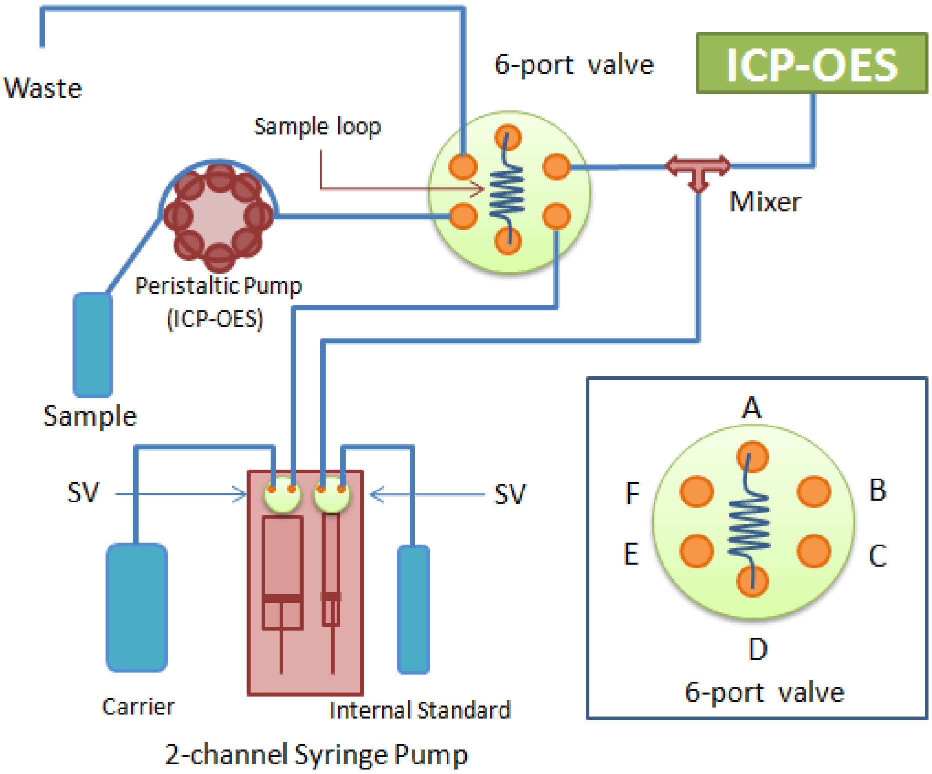
Table 4.1 Automatic system specification and ICP-OES operating conditions

Condition	Setting
Flow rate of solution loading into syringes in 2-channel syringe pump (5.00 mL and 100 µL) (mL min^{-1})	6.41
Nebulizer type	Concentric
Spray chamber type	Cyclonic
RF power (kW)	1.150
Auxiliary argon flow (L min^{-1})	0.5
Nebulizer gas flow (L min^{-1})	0.50
Coolant gas flow (L min^{-1})	12
Peristaltic pump rate (for sample loading to sample loop) (rpm)	50
Plasma view	Axial
Analysis maximum integration time[a] (s)	
- Low wavelength range[b]	10
- High wavelength range[c]	5

[a] The maximum time for detection signal integration

[b] Analytical wavelengths 167-230 nm

[c] Analytical wavelengths 200-847 nm



Scheme 4.1 Automatic on-line internal standard addition system (SV = solenoid valve).

The flow rate for solution introduction to ICP-OES, controlled by the 2-channel syringe pump is not given in Table 4.1 since its effect on the analysis was further investigated and described in topic 4.1.3.

4.1.2 Selection of analytical wavelength

Selected analytical wavelengths must provide high sensitivity and selectivity of the determination of target metals. Measurement results obtained at selected wavelength should not be interfered by the emission of neighboring lines of the other metals which were simultaneously analyzed. The specific analytical wavelengths in this research are listed in Table 4.2.

Table 4.2 Metals determined by ICP-OES in this study and their analytical wavelengths

Metals	Wavelengths (nm)
Chromium	283.5, 357.8
Copper	224.7, 324.7
Manganese	191.5, 257.6
Nickel	352.4
Yttrium	224.3, 320.3

4.1.3 Effect of solution introduction flow rate

The detection signal depended on the solution introduction flow rate. Therefore, a change of flow rate during the analysis would affect the analytical results obtained, and hence, the accuracy of the results. With a high introduction flow rate, a high amount of analyte per time unit would be detected by ICP-OES, and so the analysis was higher, compared to the results with low introduction flow rate.

The effect of solution introduction flow rate was investigated. Using the automatic system, for each flow rate, the progress of time-based signal was observed in time scan signal mode. An example is shown in Figure 4.1. These data would be used to set the analysis time interval as set in normal operation of ICP-OES.

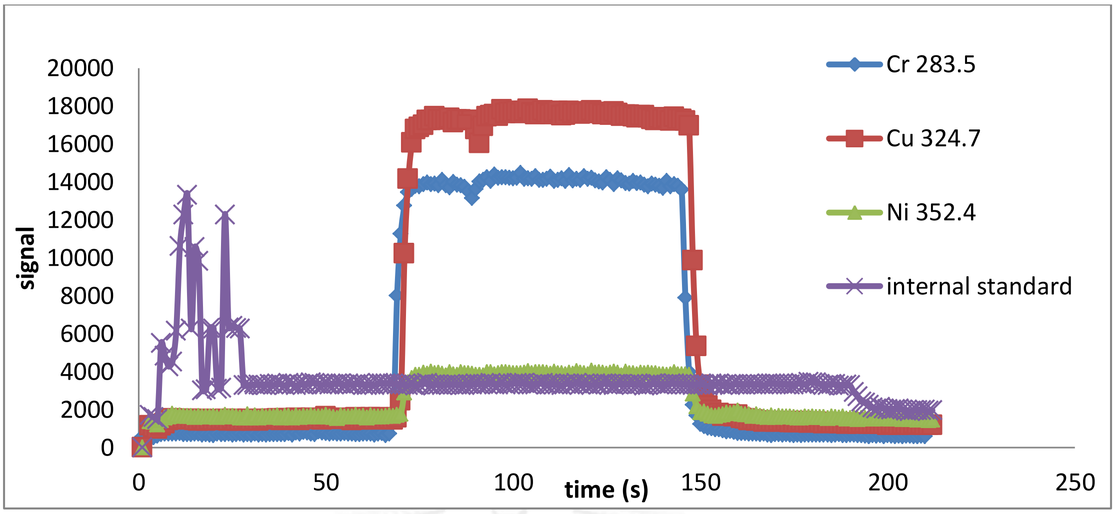


Figure 4.1 The time scan signal of 1.00 mg L^{-1} multi-element solution introduced to ICP-OES with a flow rate of 1.00 mL min^{-1}.

The yttrium signal fluctuated at the beginning of the analysis before reaching its stable signal region, indicating that the mixing of carrier solution with yttrium solution did not occur properly at the beginning. The signal of yttrium approached stable and constant values thereafter revealing the good mixing of sample and yttrium solution in the line. On the other hand, the other metals signal sharply increased and attained their stable signal region shortly. By the time that metal sample reached the mixer, the good mixing with yttrium solution had already been achieved. Finally, all signals went down as all of sample was passed through ICP-OES.

The trend of signal progress could be divided into 3 regions: 1) the unstable signal region, 2) the constant signal region, and 3) the dropping signal region that are summarized in Table 4.3.

Table 4.3 The timing of signal progress in time scan mode

Flow rate (mL min^{-1})	Metal	Start time to end time (s)		
		Unstable signal region	Constant signal region	Dropping signal region
1.00	Y	0-30	31-187	> 187
	Others	0-55	56-150	> 150
1.50	Y	0-18	19-120	> 120
	Others	0-25	26-105	> 105
2.00	Y	0-13	14-78	> 78
	Others	0-20	21-94	> 94

According to the presented results, ICP-OES operating sequences were set up in the same pattern as that of the normal operating condition. The time of the unstable signal region or the time that the metal sample did not reach constant signal region was assigned as the sample flushing time and the time of constant signal region as the analysis time in ICP-OES operation.

The effect of metal solution and internal standard solution introduction flow rate controlled by 2-channel syringe pump in the range of 1.00-2.00 mL min^{-1} on the signal of metals and the signal ratio between metals and yttrium is exhibited in the following figures. The selected analytical wavelengths were 283.5 nm for Cr, 224.7 nm for Cu, 257.6 nm for Mn, 352.4 nm for Ni, and 320.3 nm for Y.

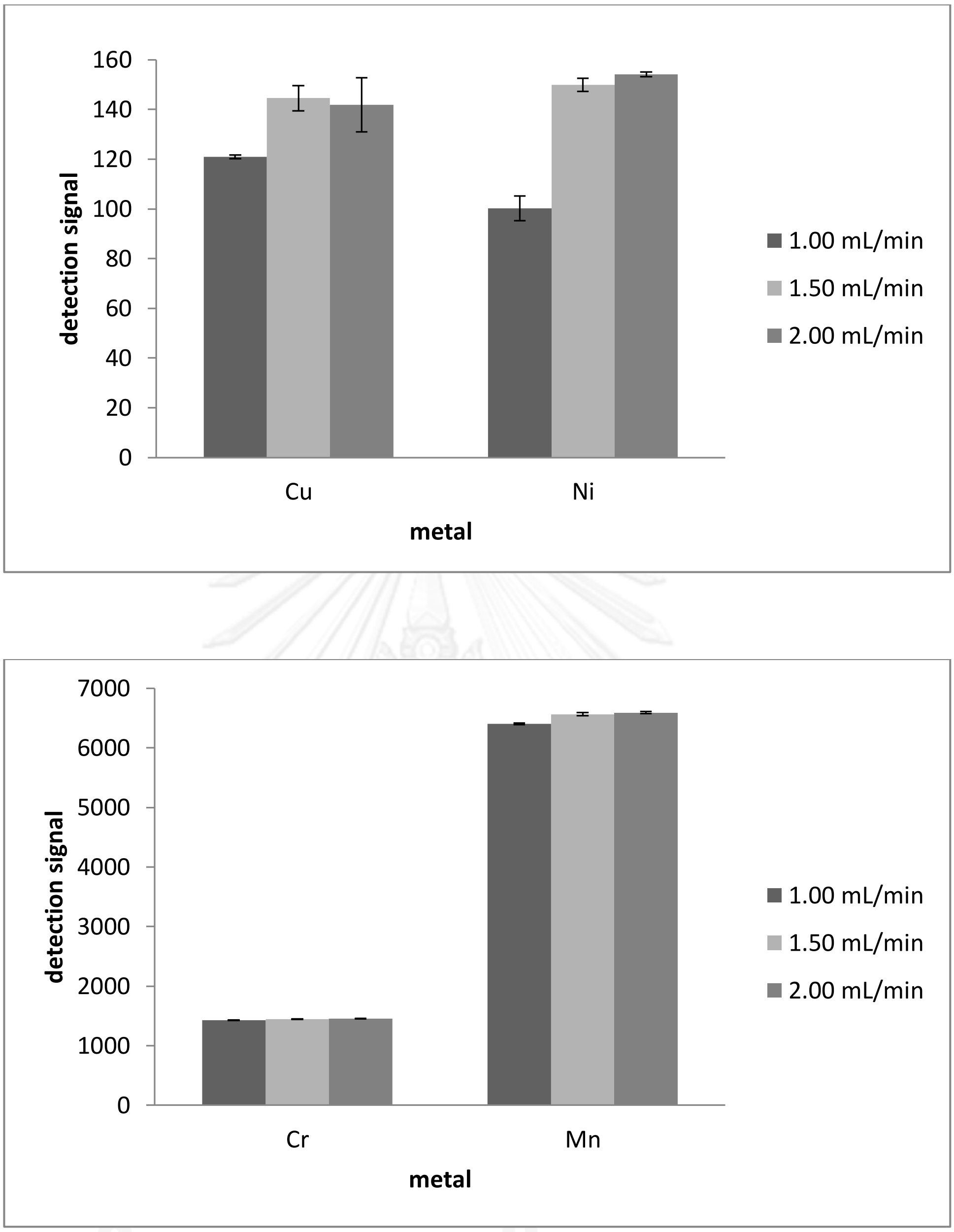
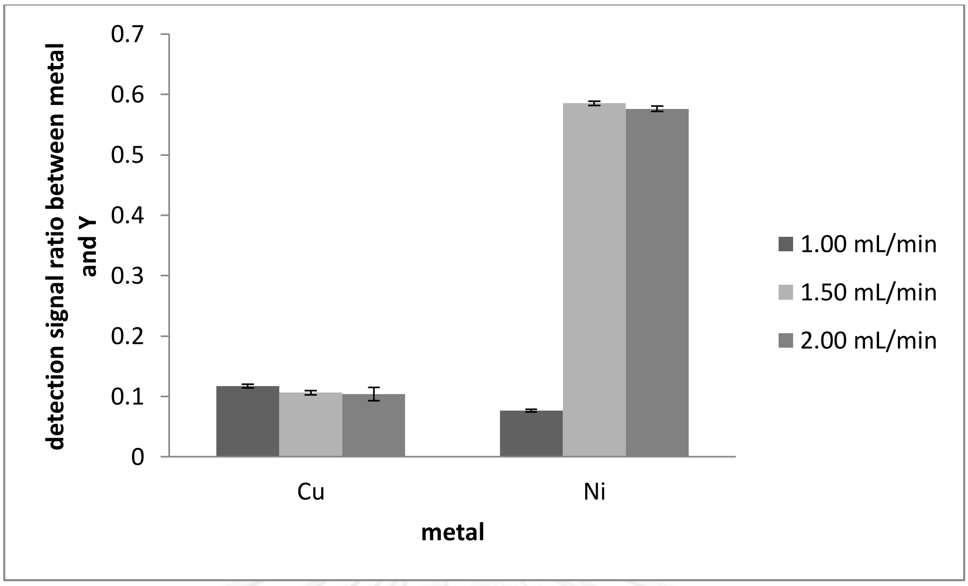


Figure 4.2 The signal of 0.10 mg L^{-1} multi-element solution observed at different introduction flow rate.



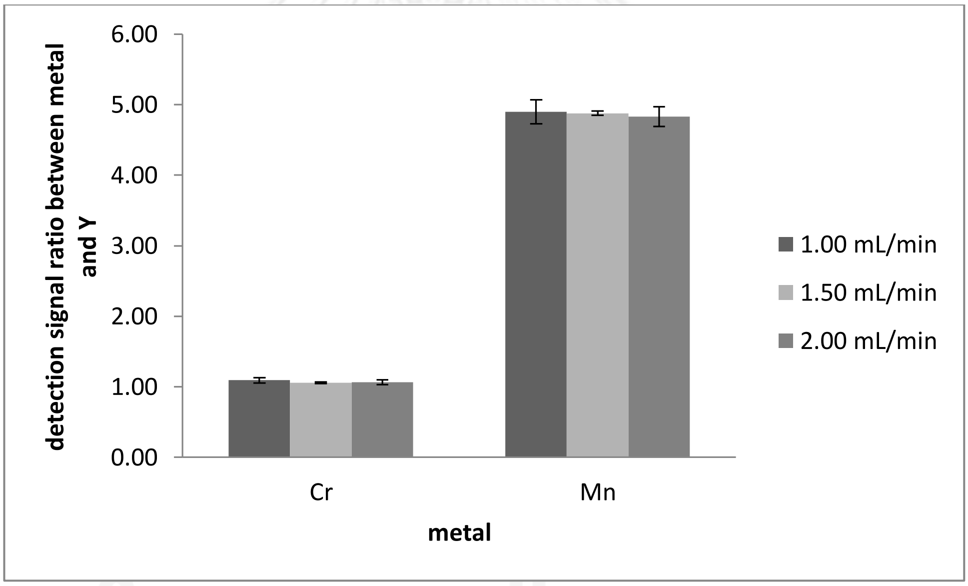
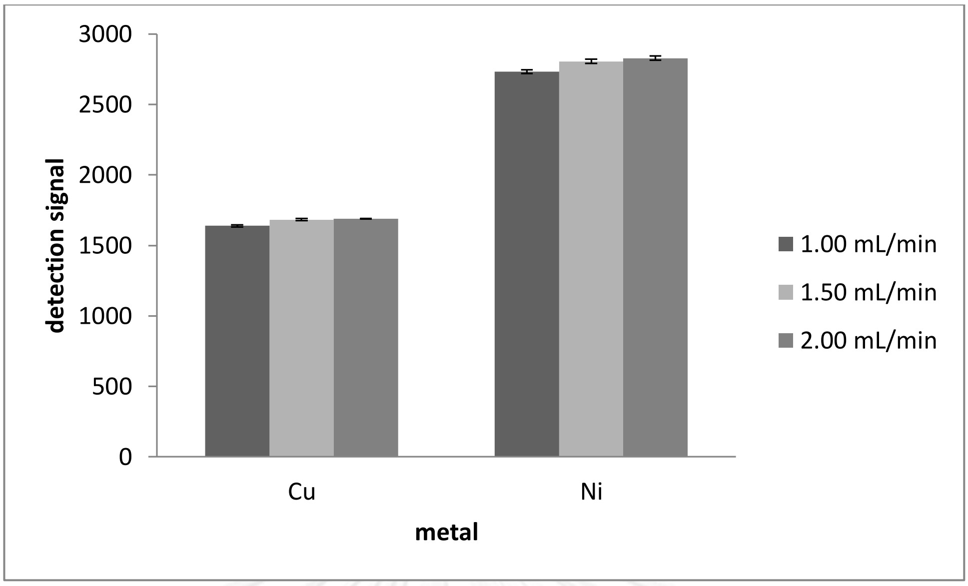


Figure 4.3 The signal ratio of metal in 0.10 mg L^{-1} multi-element solution and yttrium observed at different introduction flow rate.



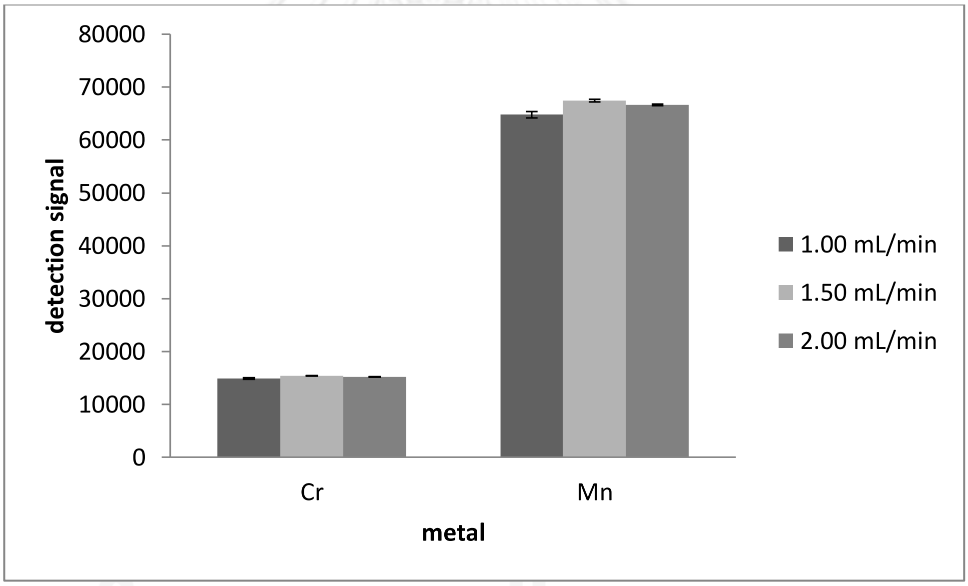
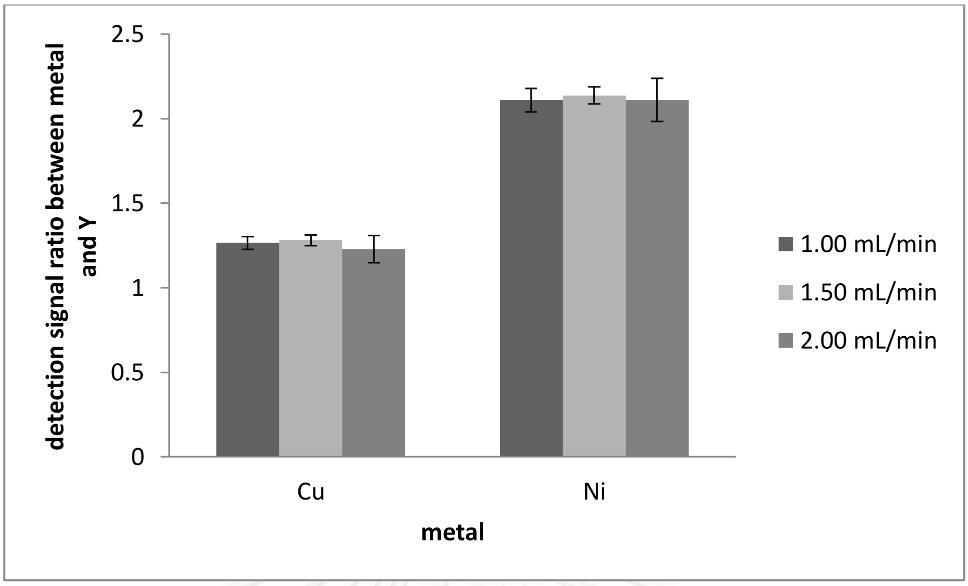


Figure 4.4 The signal of 1.00 mg L^{-1} multi-element solution observed at different introduction flow rate.



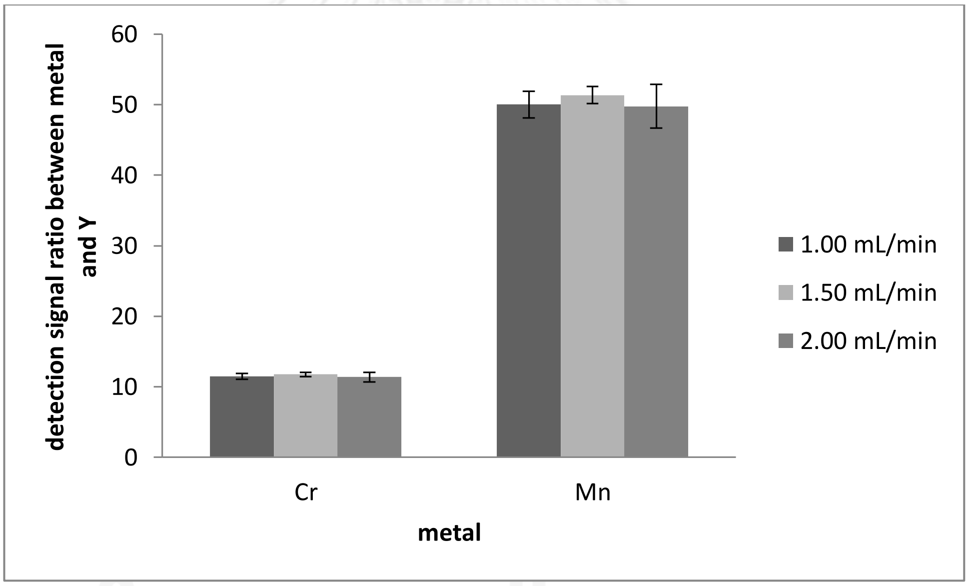


Figure 4.5 The signal ratio of metal in 1.00 mg L^{-1} multi-element solution and yttrium observed at different introduction flow rate.

The metals signal increased after increasing flow rate, revealing that a change in introduction flow rate would affect the analysis results. However, when considered the signal ratio between metals and yttrium, the change in flow rate did not lead to the significant difference in signal ratio (95% confidential level). These results indicate that the internal standard method could overcome the errors that may cause by the drift in sample introduction flow.

The results observed at the solution introduction flow rate of 1.50 and 2.00 mL min^{-1} were not significantly different at the 95% confidential level probably due to the limited efficiency of nebulization when a constant nebulization gas flow was used. As the result, although the solution introduction flow rate was increased, the detection signal remained unchanged because the increasing amount of sample per time unit was not nebulized and passed through the plasma but drained from the spray chamber instead. Nevertheless, using flow rate at 2.00 mL min^{-1}, despite the high sample throughput, a high backpressure could be generated in line that led to the solution leak in the system, in particular at mixer junction. The flow rate of 1.50 mL min^{-1} was chosen due to the lower backpressure, although, it provided lower sample throughput. In addition, it would extend the 2-channel syringe pump's life time.

The solution introduction flow rate at 1.50 mL min^{-1} was employed in further experiments. In Table 4.4, the timing and sequence of automatic system operation at this flow rate are given.

Table 4.4 The timing and sequence of system operation at flow rate of 1.50 mL min^{-1}

Number of step	Step	Duration (s)
1	Sample and solution loading	180
2	Sample flushing	30
3	Analysis	60
4	Cleaning	60

The sample throughput was 11 samples per hour.

4.1.4 Method validation

After the suitable condition for determination of metals by ICP-OES coupled to the automatic system was obtained, the linear range of the method was observed. The results are shown in Table 4.5. As expected for the determination of metals by ICP-OES, the wide linear range was achieved.

Table 4.5 Linear range of the method for determination of metals in aqueous sample by ICP-OES observed at different wavelength

Metals-analytical wavelength (nm)	**Linear range ($\mu g\ L^{-1}$)**
Cr-283.5	25.0-10,000
Cr-357.8	163.0-10,000
Cu-224.7	106.0-10,000
Cu-324.7	41.0-10,000
Mn-191.5	161.0-10,000
Mn-257.6	8.0-10,000
Ni-352.4	20.0-10,000

The method was validated by demonstrating the performance related to interday and intraday precision of the analysis, presented in term of %RSD of slope of linear equations from calibration curves. Limit of detection (LOD) and limit of quantification (LOQ) were also determined (Table 4.6). The results suggested that this method would produce results with good precision, according to the widely used criteria in Table 4.7.

Table 4.6 Precision, LOD, and LOQ of the method for determination of metals in aqueous samples by ICP-OES observed at different wavelength

Metals-analytical wavelength (nm)	RSD of slope (%)		LOD[c] (µg L^{-1})	LOQ[d] (µg L^{-1})
	Intraday[a]	Interday[b]		
Cr-283.5	5.2	17.3	4.3	24.1
Cr-357.8	6.3	15.2	48.9	162.7
Cu-224.7	5.1	12.3	30.0	105.4
Cu-324.7	9.3	10.9	6.4	40.2
Mn-191.5	9.1	11.1	61.4	160.3
Mn-257.6	0.7	2.0	2.5	7.1
Ni-352.4	1.8	5.7	4.6	19.5

[a] n = 3

[b] n = 7 within 10 days

[c] LOD = the concentration that gave the signal equal to the summation of blank signal average and three times of blank signal SD

[d] LOQ = the concentration that gave the signal equal to the summation of blank signal average and ten times of blank signal SD

Table 4.7 Acceptable values of analyte recovery and precision (%RSD) for the determination of analyte at different concentrations [29]

Unit	Mean recovery (%)	RSD (%)
100 ppm	90-107	5.3
10 ppm	80-110	7.3
1 ppm	80-110	11
100 ppb	80-110	15
10 ppb	60-115	21
1 ppb	40-120	30

Moreover, the results from the automatic system were compared with the results obtained from direct injection of standard solutions (2.0-10,000 µg L^{-1}) prepared by adding internal standard manually to ICP-OES (Table 4.8).

Table 4.8 Precision of the calibration curves obtained by direct injection for determination of metals in aqueous samples by ICP-OES

Metals-analytical wavelength (nm)	RSD of slope[a] (%)
Cr-283.5	5.0
Cr-357.8	5.8
Cu-224.7	4.7
Cu-324.7	9.1
Mn-191.5	8.2
Mn-257.6	2.3
Ni-352.4	1.9

[a] n = 3

The results indicated that the performance of both methods was not significantly different at the 95% confidential level. However, using the automatic system is less laborious.

4.1.5 Analysis of water samples

The determination of metals in real water samples (drinking water, pool water, tap water, river water, and wastewater) by ICP-OES coupled to the automatic internal standard addition system was performed using spiked method. The accuracy of the results presented as %recovery is exhibited.

The recoveries were calculated obeyed Equation 1;

$$recovery\,(\%) = \frac{C_c - C_b}{C_s} \times 100 \qquad (1)$$

where C_c is the concentration of spiked sample calculated from calibration curve

C_b is the concentration of non-spiked sample calculated from calibration curve

C_s is the concentration added into sample

Table 4.9 Determination of Cr, Cu, Mn, and Ni in drinking water by internal standard method via the automatic system

Added (μg L^{-1})	Metals-analytical wavelength (nm)					
	Cr-283.5			Cu-224.7		
	Found^{a} (μg L^{-1})	RSD^{a} (%)	Recovery^{a} (%)	Found^{a} (μg L^{-1})	RSD^{a} (%)	Recovery^{a} (%)
-	n.d.	-	-	n.d.	-	-
3	n.d.	-	-	n.d.	-	-
5	n.d.	-	-	n.d.	-	-
9	n.d.	-	-	n.d.	-	-
30	31.0 ±0.9	2.9	103.3	n.d.	-	-
50	54.0 ± 2.8	5.2	108.0	n.d.	-	-
90	96.8 ± 1.9	2.0	107.5	n.d.	-	-
300	295.3 ± 1.5	0.5	98.4	281.1 ± 2.8	1.0	93.7
500	498.7 ± 1.1	0.2	99.7	475.2 ± 0.6	0.1	95.0
900	891.1 ± 5.9	0.7	99.0	846.8 ± 6.1	0.7	94.1
3000	3101.9 ± 101.6	3.3	103.4	2978.5 ± 94.8	3.2	99.3
5000	5038.6 ± 56.2	1.1	100.8	5098.4 ± 10.4	0.2	102.0
9000	8913.0 ± 19.4	0.2	99.0	9073.4 ± 44.3	0.5	100.8

Table 4.9 Determination of Cr, Cu, Mn, and Ni in drinking water by internal standard method via the automatic system (cont.)

Added (µg L^{-1})	Metals-analytical wavelength (nm)					
	Mn-257.6			Ni-352.4		
	Found[a] (µg L^{-1})	RSD[a] (%)	Recovery[a] (%)	Found[a] (µg L^{-1})	RSD[a] (%)	Recovery[a] (%)
-	n.d.	-	-	n.d.	-	-
3	n.d.	-	-	n.d.	-	-
5	n.d.	-	-	n.d.	-	-
9	8.9 ± 0.3	3.4	98.9	n.d.	-	-
30	31.2 ± 0.4	1.3	104.0	30.2 ± 0.7	2.3	100.7
50	52.4 ± 3.7	7.1	104.8	52.3 ± 1.4	2.7	104.6
90	93.8 ± 1.3	1.4	104.2	101.0 ± 11.54	11.4	112.2
300	287.8 ± 1.2	0.4	95.9	321.7 ± 1.5	0.5	107.2
500	485.5 ± 1.5	0.3	97.1	530.1 ± 2.9	0.6	106.0
900	870.0 ± 4.9	0.6	96.7	938.2 ± 12.1	1.3	104.2
3000	3103.8 ± 7.1	0.2	103.5	3064.2 ± 54.4	1.8	102.1
5000	4942.5 ± 28.0	0.6	98.9	5029.0 ± 23.9	0.5	100.6
9000	9052.8 ± 38.6	0.4	100.6	9029.8 ± 18.1	0.2	100.3

[a] mean ± SD (n=3)

n.d. = non detectable

Table 4.10 Determination of Cr, Cu, Mn, and Ni in pool water by internal standard method via the automatic system

Added (µg L^{-1})	Metals-analytical wavelength (nm)					
	Cr-283.5			Cu-224.7		
	Found[a] (µg L^{-1})	RSD[a] (%)	Recovery[a] (%)	Found[a] (µg L^{-1})	RSD[a] (%)	Recovery[a] (%)
-	n.d.	-	-	n.d.	-	-
3	n.d.	-	-	n.d.	-	-
5	n.d.	-	-	n.d.	-	-
9	n.d.	-	-	n.d.	-	-
30	30.6 ± 0.6	2.0	102.0	n.d.	-	-
50	52.8 ± 0.3	0.6	105.6	n.d.	-	-
90	91.3 ± 5.6	6.1	101.4	n.d.	-	-
300	284.0 ± 0.9	0.3	94.7	272.6 ± 0.7	0.3	90.9
500	477.6 ± 1.4	0.3	95.5	455.9 ± 1.6	0.4	91.2
900	855.9 ± 9.6	1.1	95.1	822.9 ± 2.0	0.2	91.4
3000	2929.1 ± 146.8	5.0	97.6	2856.3 ± 52.1	1.8	95.2
5000	5028.3 ± 120.0	2.4	100.6	5051.4 ± 38.3	0.8	101.0
9000	9141.4 ± 148.8	1.6	101.6	9256.3 ± 133.6	1.4	102.8

Table 4.10 Determination of Cr, Cu, Mn, and Ni in pool water by internal standard method via the automatic system (cont.)

Added (µg L^{-1})	Metals-analytical wavelength (nm)					
	Mn-257.6			Ni-352.4		
	Found[a] (µg L^{-1})	RSD[a] (%)	Recovery[a] (%)	Found[a] (µg L^{-1})	RSD[a] (%)	Recovery[a] (%)
-	n.d.	-	-	n.d.	-	-
3	n.d.	-	-	n.d.	-	-
5	n.d.	-	-	n.d.	-	-
9	8.9 ± 0.5	5.6	98.9	n.d.	-	-
30	30.1 ± 2.2	7.3	100.3	31.0 ± 0.4	1.3	103.3
50	51.1 ± 2.4	4.7	102.2	52.3 ± 3.5	6.7	105.0
90	90.3 ± 7.2	8.0	100.3	88.2 ± 3.8	4.3	98.0
300	281.2 ± 1.2	0.4	93.7	315.1 ± 6.2	2.0	105.0
500	473.5 ± 1.3	0.3	94.7	514.9 ± 5.7	1.1	103.0
900	855.5 ± 7.4	0.9	95.1	911.2 ± 12.7	1.4	101.2
3000	2984.3 ± 54.5	1.8	99.5	2906.6 ± 172.1	5.9	96.9
5000	5081.0 ± 39.6	0.8	101.6	5021.0 ± 65.2	1.3	100.4
9000	9259.8 ± 139.1	1.5	102.9	8869.7 ± 156.2	1.8	98.6

[a] mean ± SD (n=3)

n.d. = non detectable

Table 4.11 Determination of Cr, Cu, Mn, and Ni in tap water by internal standard method via the automatic system

Added (µg L^{-1})	Metals-analytical wavelength (nm)					
	Cr-283.5			Cu-224.7		
	Found[a] (µg L^{-1})	RSD[a] (%)	Recovery[a] (%)	Found[a] (µg L^{-1})	RSD[a] (%)	Recovery[a] (%)
-	n.d.	-	-	n.d.	-	-
3	n.d.	-	-	n.d.	-	-
5	n.d.	-	-	n.d.	-	-
9	n.d.	-	-	n.d.	-	-
30	30.3 ± 1.2	3.9	101.1	n.d.	-	-
50	50.3 ± 1.8	3.6	100.6	n.d.	-	-
90	90.8 ± 4.3	4.7	100.9	n.d.	-	-
300	288.1 ± 1.0	0.4	96.0	268.9 ± 6.3	2.3	89.6
500	487.7± 2.0	0.4	97.5	459.1 ± 0.7	0.2	91.8
900	879.6 ± 3.0	0.3	97.7	826.5 ± 2.6	0.3	91.8
3000	2911.8 ± 47.1	1.6	97.1	3051.9 ± 61.7	3.0	101.7
5000	5044.6 ± 55.5	1.1	100.9	4811.9 ± 70.0	1.5	96.2
9000	8978.2 ± 194.0	2.2	99.8	9439.6 ± 57.2	0.6	104.9

Table 4.11 Determination of Cr, Cu, Mn, and Ni in tap water by internal standard method via the automatic system (cont.)

Added (µg L^{-1})	Metals-analytical wavelength (nm)					
	Mn-257.6			Ni-352.4		
	Found^{a} (µg L^{-1})	RSD^{a} (%)	Recovery^{a} (%)	Found^{a} (µg L^{-1})	RSD^{a} (%)	Recovery^{a} (%)
-	n.d.	-	-	n.d.	-	-
3	n.d.	-	-	n.d.	-	-
5	n.d.	-	-	n.d.	-	-
9	9.8 ± 0.6	5.9	108.4	n.d.	-	-
30	31.1 ± 2.5	7.9	103.7	32.2 ± 4.3	13.4	107.3
50	53.4 ± 3.0	5.6	106.8	53.8 ± 3.7	7.0	107.6
90	84.0 ± 4.2	4.9	93.3	97.93 ± 4.9	5.0	108.8
300	282.5 ± 1.4	0.5	94.2	324.1 ± 2.9	0.9	108.0
500	478.2 ± 1.7	0.3	95.6	529.3 ± 3.6	0.7	105.9
900	866.0 ± 2.2	0.3	96.2	932.1 ± 4.1	0.4	103.6
3000	3141.4 ± 152.2	4.8	104.7	3091.7 ± 98.1	3.2	103.1
5000	5131.7 ± 48.9	0.9	102.6	5147.7 ± 118.0	2.3	103.0
9000	8678.1 ± 219.1	2.5	96.4	9104.6 ± 61.2	0.7	101.2

[a] mean ± SD (n=3)

n.d. = non detectable

Table 4.12 Determination of Cr, Cu, Mn, and Ni in river water by internal standard method via the automatic system

Added (µg L^{-1})	Metals-analytical wavelength (nm)					
	Cr-283.5			Cu-224.7		
	Found[a] (µg L^{-1})	RSD[a] (%)	Recovery[a] (%)	Found[a] (µg L^{-1})	RSD[a] (%)	Recovery[a] (%)
-	n.d.	-	-	n.d.	-	-
3	n.d.	-	-	n.d.	-	-
5	n.d.	-	-	n.d.	-	-
9	n.d.	-	-	n.d.	-	-
30	32.7 ± 2.3	7.0	108.9	n.d.	-	-
50	51.0 ± 1.5	2.9	102.0	n.d.	-	-
90	92.3 ± 2.6	2.8	102.6	n.d.	-	-
300	287.9 ± 0.7	0.3	96.0	273.4 ± 1.6	0.6	91.1
500	477.9 ± 1.8	0.4	95.6	486.6 ± 3.5	0.7	97.1
900	860.5 ± 2.0	0.2	95.6	826.1 ± 2.1	0.3	91.8
3000	3038.9 ± 55.1	1.8	101.3	3060.9 ± 53.3	1.7	102.0
5000	5179.0 ± 66.4	1.3	103.6	5056.0 ± 45.4	0.9	101.1
9000	9022.7 ± 19.8	0.2	100.3	8957.1 ± 48.3	0.5	99.5

Table 4.12 Determination of Cr, Cu, Mn, and Ni in river water by internal standard method via the automatic system (cont.)

Added (μg L^{-1})	Metals-analytical wavelength (nm)					
	Mn-257.6			Ni-352.4		
	Found^{a} (μg L^{-1})	RSD^{a} (%)	Recovery^{a} (%)	Found^{a} (μg L^{-1})	RSD^{a} (%)	Recovery^{a} (%)
-	n.d.	-	-	n.d.	-	-
3	n.d.	-	-	n.d.	-	-
5	n.d.	-	-	n.d.	-	-
9	9.0 ± 0.5	5.8	99.8	n.d.	-	-
30	30.7 ± 1.5	4.9	102.4	33.3 ± 1.7	5.2	111.0
50	53.5 ± 1.0	1.8	107.0	52.9 ± 3.1	5.9	105.9
90	95.3 ± 1.1	1.2	105.9	93.8 ± 2.4	2.6	104.2
300	281.4 ± 0.5	0.2	93.8	316.3 ± 1.8	0.6	105.4
500	468.6 ± 2.2	0.5	93.7	505.2 ± 3.8	0.7	101.0
900	851.3 ± 2.1	0.2	94.6	905.7 ± 2.5	0.3	100.6
3000	3187.4 ± 79.7	2.5	106.2	3106.3 ± 91.3	2.9	103.5
5000	4985.9 ± 109.4	2.2	99.7	4962.6 ± 123.6	2.5	99.3
9000	9337.4 ± 287.6	3.1	103.7	9027.9 ± 6.4	0.1	100.3

^{a}mean ± SD (n=3)

n.d. = non detectable

Table 4.13 Determination of Cr, Cu, Mn, and Ni in wastewater by internal standard method via the automatic system

Added (µg L^{-1})	Metals-analytical wavelength (nm)					
	Cr-283.5			Cu-224.7		
	Found[a] (µg L^{-1})	RSD[a] (%)	Recovery[a] (%)	Found[a] (µg L^{-1})	RSD[a] (%)	Recovery[a] (%)
-	n.d.	-	-	n.d.	-	-
3	n.d.	-	-	n.d.	-	-
5	n.d.	-	-	n.d.	-	-
9	n.d.	-	-	n.d.	-	-
30	32.4 ± 3.6	11.1	108.0	n.d.	-	-
50	53.0 ± 1.5	2.9	106.1	n.d.	-	-
90	93.9 ± 1.6	1.7	104.3	n.d.	-	-
300	268.5 ± 3.8	1.4	89.5	257.7 ± 1.9	0.8	85.9
500	456.9 ± 13.6	3.0	91.4	431.8 ± 4.2	1.0	86.4
900	820.1 ± 2.5	0.3	91.1	774.5 ± 16.1	2.1	86.1
3000	3141.3 ± 52.3	1.7	104.7	2922.1 ± 50.7	1.7	97.4
5000	5214.1 ± 17.6	0.3	104.3	5103.1 ± 97.9	1.9	102.1
9000	8754.6 ± 50.4	0.6	97.3	9064.5 ± 36.8	0.4	100.7

Table 4.13 Determination of Cr, Cu, Mn, and Ni in wastewater by internal standard method via the automatic system (cont.)

Added (µg L^{-1})	**Metals-analytical wavelength (nm)**					
	Mn-257.6			**Ni-352.4**		
	Found[a] (µg L^{-1})	**RSD[a] (%)**	**Recovery[a] (%)**	**Found[a] (µg L^{-1})**	**RSD[a] (%)**	**Recovery[a] (%)**
-	n.d.	-	-	n.d.	-	-
3	n.d.	-	-	n.d.	-	-
5	n.d.	-	-	n.d.	-	-
9	10.0 ± 0.6	6.1	111.5	n.d.	-	-
30	31.7 ± 0.7	2.2	105.7	32.0 ± 1.8	5.6	106.8
50	50.3 ± 2.8	5.5	100.6	51.1 ± 3.3	6.5	102.1
90	84.0 ± 1.4	1.7	93.4	88.2 ± 2.6	3.0	98.0
300	258.4 ± 8.0	3.1	86.1	305.8 ± 4.7	1.5	101.9
500	438.6 ± 12.4	2.8	87.7	507.8 ± 32.2	6.3	101.6
900	790.5 ± 2.0	0.3	87.8	877.5 ± 3.3	0.4	97.5
3000	3136.4 ± 57.3	1.8	104.5	3003.7 ± 103.8	3.5	100.1
5000	4497.9 ± 193.5	4.3	90.0	5209.2 ± 277.6	5.3	104.2
9000	9315.9 ± 241.7	2.6	103.5	9186.1 ± 72.1	0.8	102.1

[a] mean ± SD (n=3)

n.d. = non detectable

The recoveries of Cr, Cu, Mn, and Ni from samples spiked with Cr, Cu, Mn, and Ni standard were in the range of 98.9-111.5 % for the concentration lower than 10 µg L^{-1} level, 93.3-112.2 % for 10-100 µg L^{-1} level, and 85.9–108.0 % for concentration higher than 100 µg L^{-1} level, revealing that the method could be applied for the determination of Cr, Cu, Mn, and Ni in water samples with acceptable accuracy.

By using the automatic system, the collected analysis results were calculated by using internal standard method and external standard method. The recoveries observed by using both analytical methods were compared (see the results in Appendix 2).

The results showed that the recoveries observed by both analytical methods were not significantly different at the 95% confidential level. It indicated that the solution introduction performed by 2-channel syringe pump provided the stability of solution flow so the detection signal was good.

4.1.6 Analysis of certified reference material

The accuracy of the method was evaluated by analyzing Cr, Cu, Mn, and Ni in certified reference material (ERM-CA022a, European Reference Materials, Union of Europe). The results are shown in Table 4.14

Table 4.14 Determination of Cr, Cu, Mn, and Ni in certified reference material

Metals-analytical wavelength (nm)	**Certified (µg L^{-1})**	**Found[a] (µg L^{-1})**	**RSD[a] (%)**	**Recovery[a] (%)**
Cr-283.5	50.8 ± 2.7	50.9 ± 2.0	4.0	100.3
Cu-224.7	2100 ± 70	2181.3 ± 53.7	2.5	103.9
Mn-257.6	52.5 ± 3.9	55.0 ± 0.7	1.3	104.8
Ni-352.4	20.5 ± 1.6	22.0 ± 0.3	1.4	107.2

[a] mean ± SD (n=3)

The values obtained by the proposed method were not significantly different from the certified values at the 95% confidential level; therefore, the method could be applied for the determination of Cr, Cu, Mn, and Ni in water samples with acceptable accuracy.

4.2 Determination of metals in oil solutions

Like the determination of metals in aqueous solution, the internal standard solution was a 5.10 µg g^{-1} yttrium in oil solution because the same 2-channel syringe pump of the automatic system which consisted of a 5-mL syringe and a 100-µL syringe was also used. The final concentration of yttrium mixed in the metal sample or standard solution was 100 ng g^{-1}.

4.2.1 Automatic system setup

The automatic system setup for the determination of metal in aqueous solutions was applied to the analysis of metal in oil solutions, (see in Scheme 4.1), except that the tube used to load solution into sample loop was made from Viton polymer and the carrier solution was Premisolv^{TM} (see the photographs of the system in Appendix 1).

Automatic system specification and ICP-OES operating conditions are listed in Table 4.15.

Table 4.15 Automatic system specification and ICP-OES operating conditions

Condition	Setting
Flow rate of solution loading into 2-channel syringe pump (5.00 mL and 100 µL) (mL min^{-1})	6.41
Nebulizer type	Concentric
Spray chamber type	Cyclonic
RF power (kW)	1.150
Auxiliary argon flow (L min^{-1})	0.5
Nebulizer gas flow (L min^{-1})	0.50
Coolant gas flow (L min^{-1})	16

Table 4.15 Automatic system specification and ICP-OES operating conditions (cont.)

Condition	Setting
Peristaltic pump rate (for sample loading to sample loop) (rpm)	50
Plasma view	Axial
Analysis maximum integration time[a] (s)	
- Low wavelength range[b]	10
- High wavelength range[c]	5

[a] The maximum time for detection signal integration

[b] Analytical wavelength 167-230 nm

[c] Analytical wavelength 200-847 nm

The solution introduction flow rate controlled by the 2-channel syringe pump and the oxygen additional gas flow rate are not specified in Table 4.15 and the effect of these two operating conditions were further investigated and described in topic 4.2.3 and 4.2.4, respectively.

4.2.2 Selection of analytical wavelength

The criteria in analytical wavelength selection was the same as explained in topic 4.1.2. The specific analytical wavelengths in this research are listed in Table 4.16.

All metals in this study are the representatives of wear metals and additive metals that could be presented in oil and are often monitored in oil samples.

Table 4.16 Metals determined by ICP-OES in this study and their analytical wavelengths

Metals	Wavelength (nm)
Aluminium	308.2
Chromium	283.5, 357.8
Copper	324.7
Iron	259.9
Lead	261.4, 283.3
Tin	242.9,
Yttrium	224.3, 324.2

4.2.3 Effect of oxygen additional gas flow rate

The oxygen was added into the plasma in order to reach a complete combustion of organic substance in oil and to eliminate carbon emission which could absorb and shield analyte signal by deposition on the ICP-OES torch.

In this part, the solution introduction flow rate of 1.50 mL min^{-1} was adopted because it was a selected operating condition for the determination of metals in aqueous sample by the automatic system. The progress of overall time-based signal from the analysis of standard oil solution was monitored and the signal changed in the similar trend as that previously observed (Figure 4.1).

The effect of oxygen additional gas flow rate in the range of 0.05-0.15 L min^{-1} on the signal of metals and the signal ratio between metals and yttrium is exhibited in the following figures. The selected analytical wavelengths were 308.2 nm for Al, 357.8 nm for Cr, 324.7 nm for Cu, 259.9 nm for Fe, 283.3 nm for Pb, 242.9 nm for Sn, and 324.2 nm for Y.

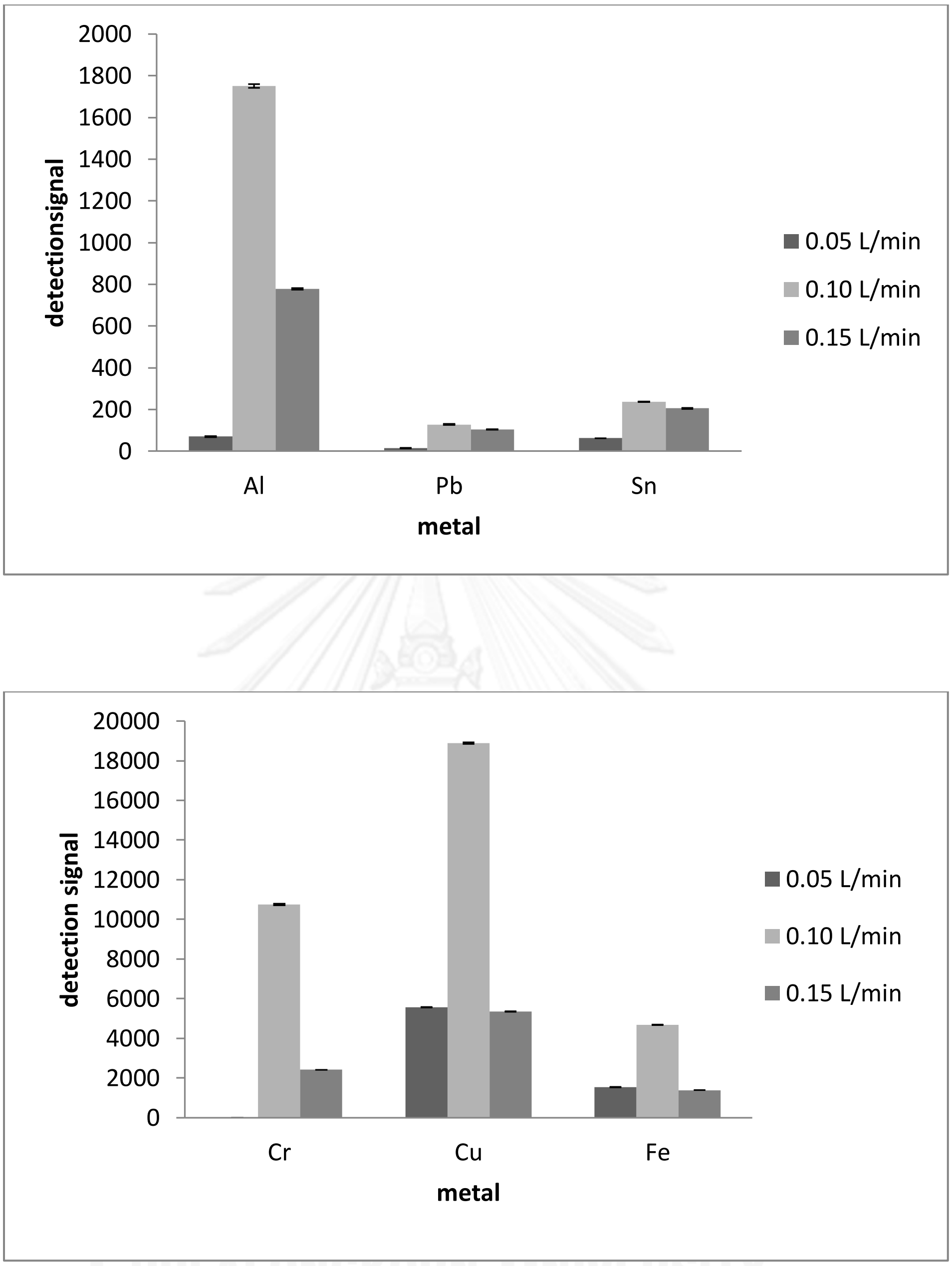
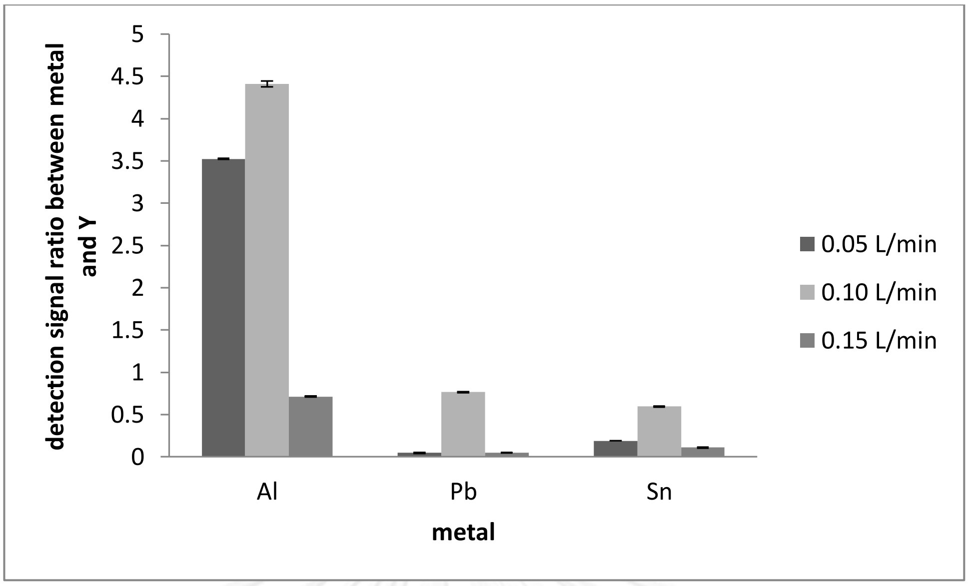


Figure 4.6 The signal of 1.00 µg g^{-1} multi-element oil solution observed at different oxygen additional gas flow rate.



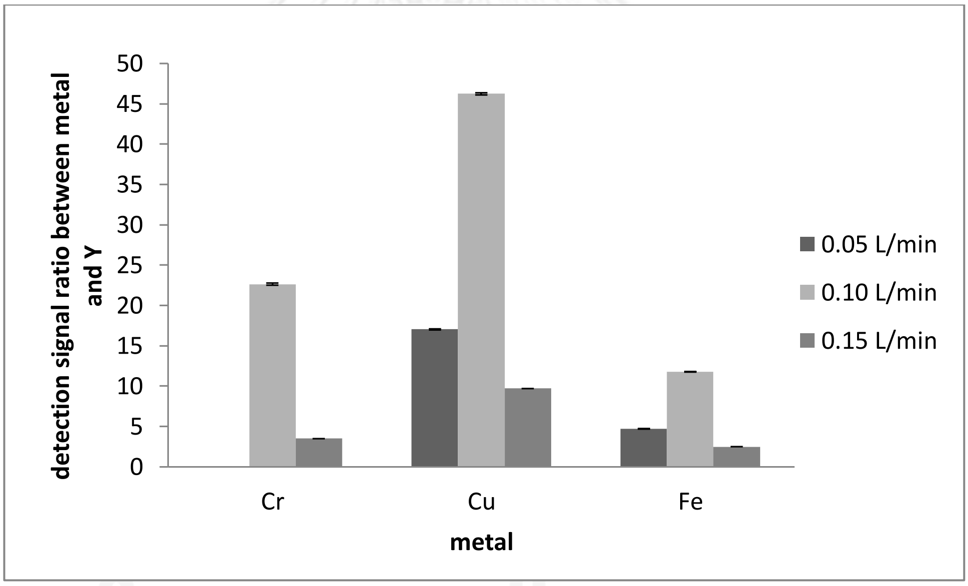
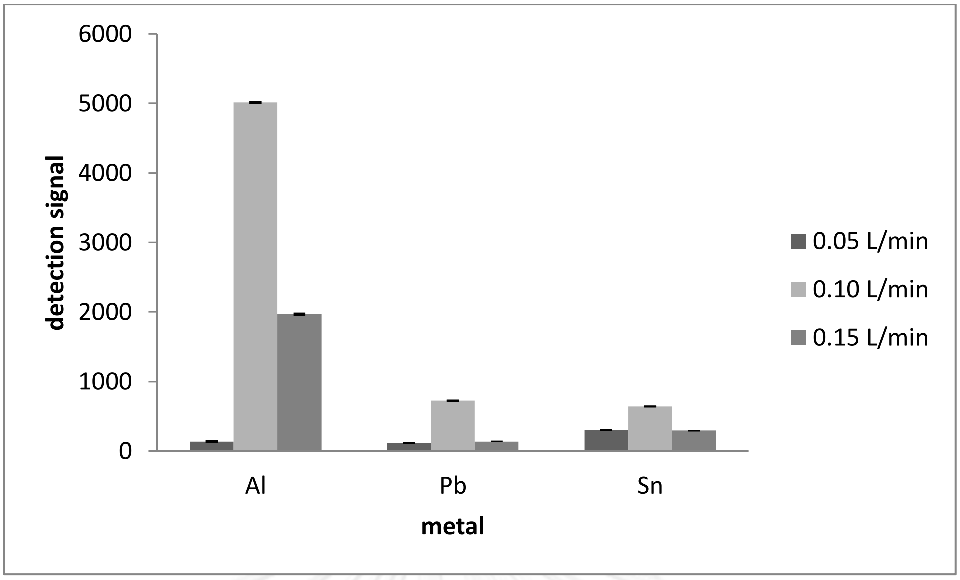


Figure 4.7 The signal ratio of metal in 1.00 μg g^{-1} multi-element oil solution and yttrium observed at oxygen additional gas flow rate.



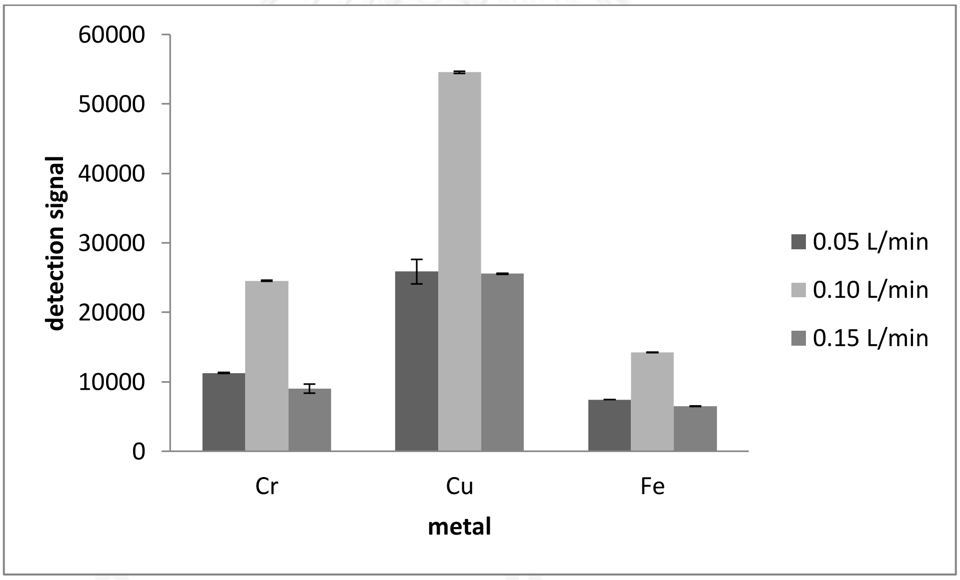
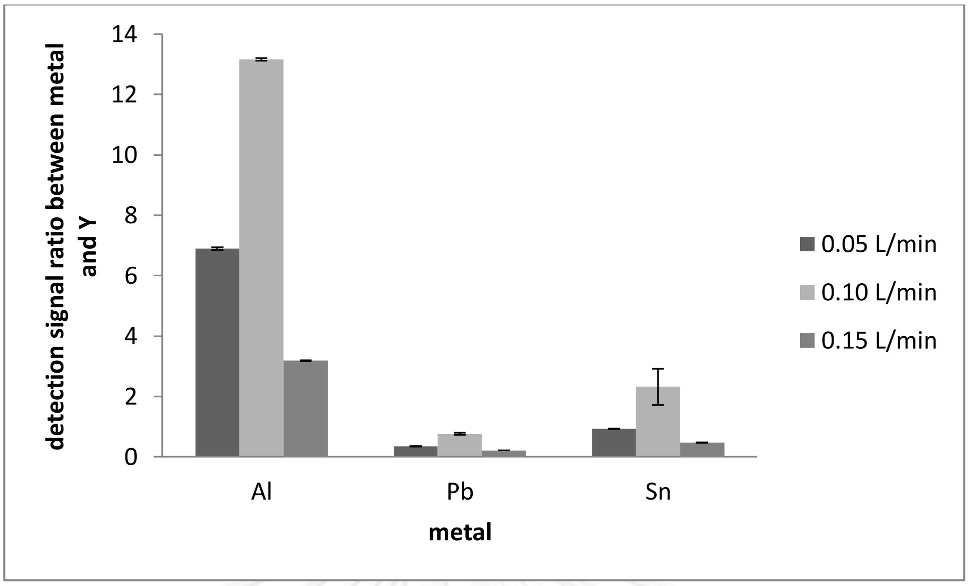


Figure 4.8 The signal of 5.00 µg g^{-1} multi-element oil solution observed at different oxygen additional gas flow rate.



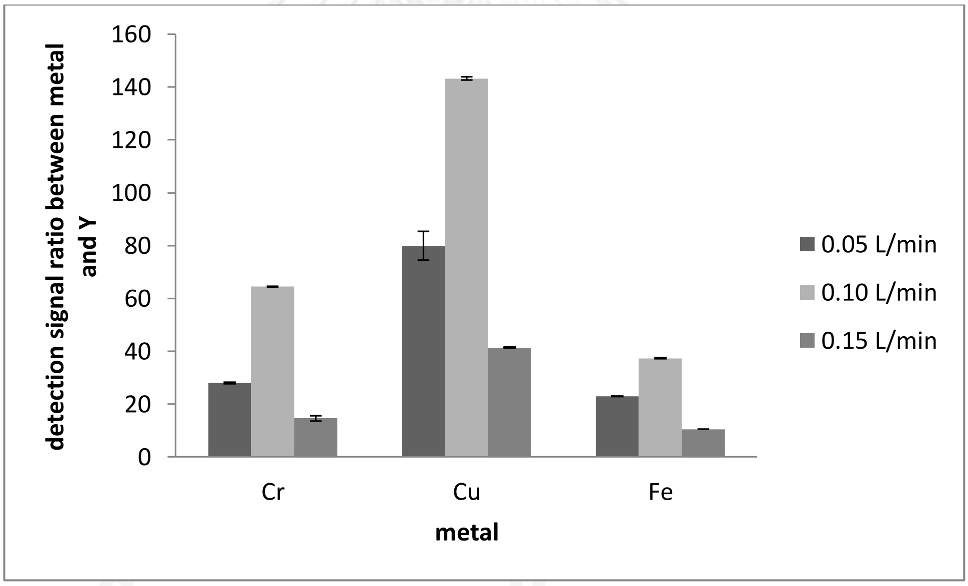


Figure 4.9 The signal ratio of metal in 5.00 µg g^{-1} multi-element oil solution and yttrium observed at different oxygen additional gas flow rate.

When flow rate of oxygen that was added in auxiliary argon gas was increased from 0.05 to 0.10 L min^{-1}, the signal intensity was enhanced because oxygen gas involved in combustion reaction and suppressed carbon emission, resulting in lower background signal. On the contrary, when oxygen flow rate was raised to 0.15 L min^{-1}, the signal intensity decreased. It is likely that a very high flow of oxygen together with flow of auxiliary gas would reduce the residence time of analyte in plasma, and hence the emission signal decreased.

It suggested that the oxygen gas was required in the determination of metal in oil sample. The system was operated with an oxygen additional gas flow rate of 0.10 L min^{-1} in further experiments.

4.2.4 Effect of solution introduction flow rate

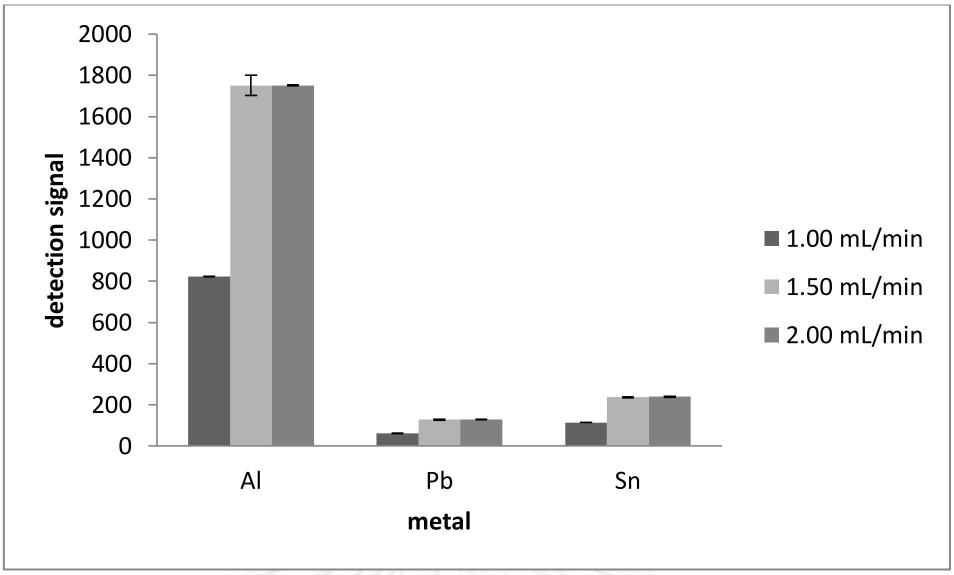
The effect of oil solution introduction flow rate was investigated. The selection of suitable flow rate was based on the criteria that it provided short analysis time and good detection sensitivity. The data from time scan signal mode collected at each flow rate (Table 4.17) were further employed to set ICP-OES operating conditions.

Table 4.17 The timing of signal progress in time scan mode

Flow rate ($mL\ min^{-1}$)	Metal	Start time to end time (s)		
		Unstable signal region	Constant signal region	Dropping signal region
1.0	Y	0-35	36-190	> 190
	Others	0-60	61-154	> 154
1.5	Y	0-25	26-125	> 125
	Others	0-36	37-111	> 111
2.0	Y	0-19	20-83	> 83
	Others	0-23	24-98	> 98

According to the summarized results, ICP-OES operating conditions were set up as normally performed condition in order to investigate the effect of solution introduction flow rate. The time of the unstable signal region of other metals was set as the sample flushing time and the time of constant signal region as the analysis time in ICP-OES operation.

The effect of solution introduction flow rate controlled by the 2-channel syringe pump in the range of 1.00-2.00 mL min^{-1} on the signal of metals and the signal ratio between metals and yttrium is exhibited in the following figures. The selected analytical wavelengths were 308.2 nm for Al, 357.8 nm for Cr, 324.7 nm for Cu, 259.9 nm for Fe, 283.3 nm for Pb, 242.9 nm for Sn, and 324.2 nm for Y.



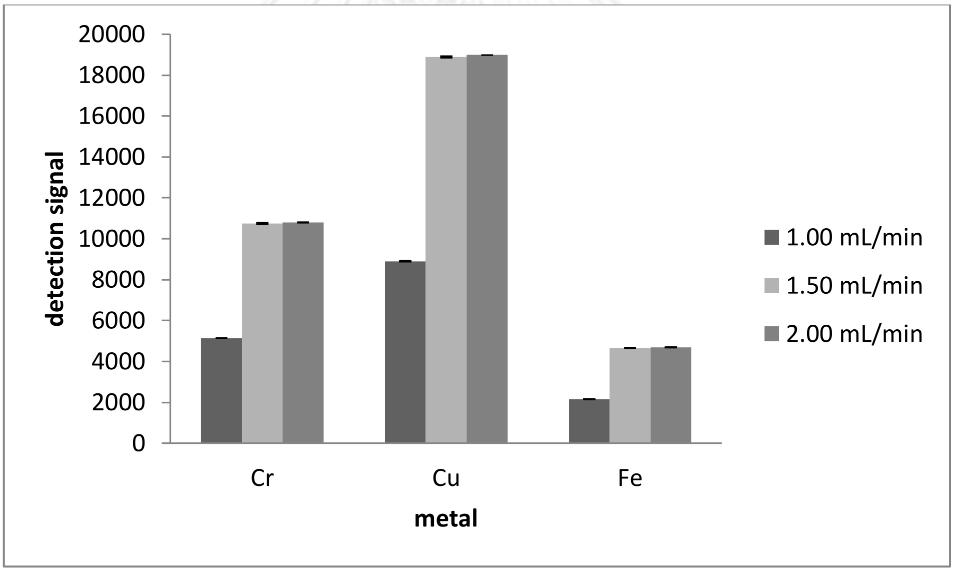
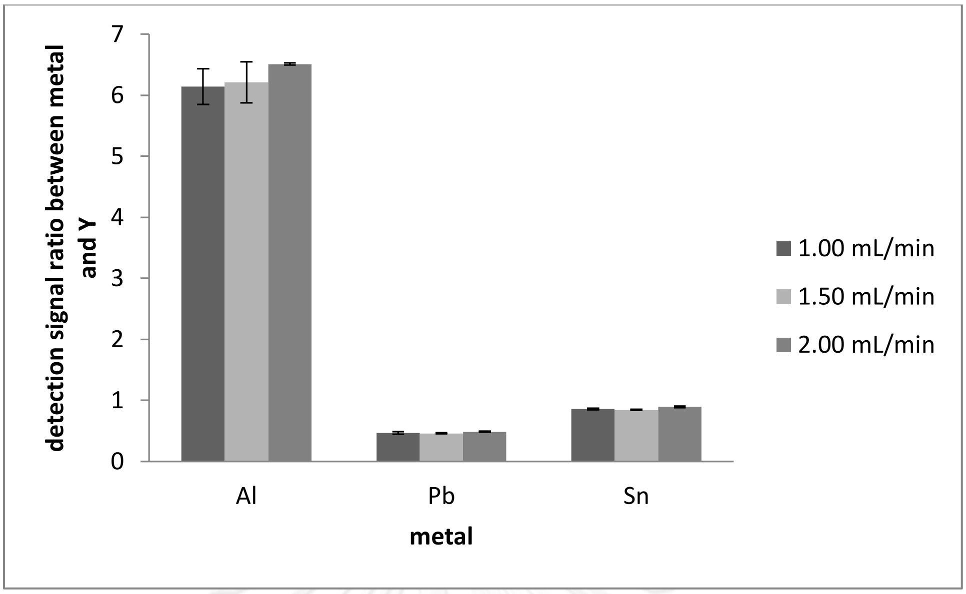


Figure 4.10 The signal of 1.00 µg g^{-1} multi-element oil solution observed at different introduction flow rate.



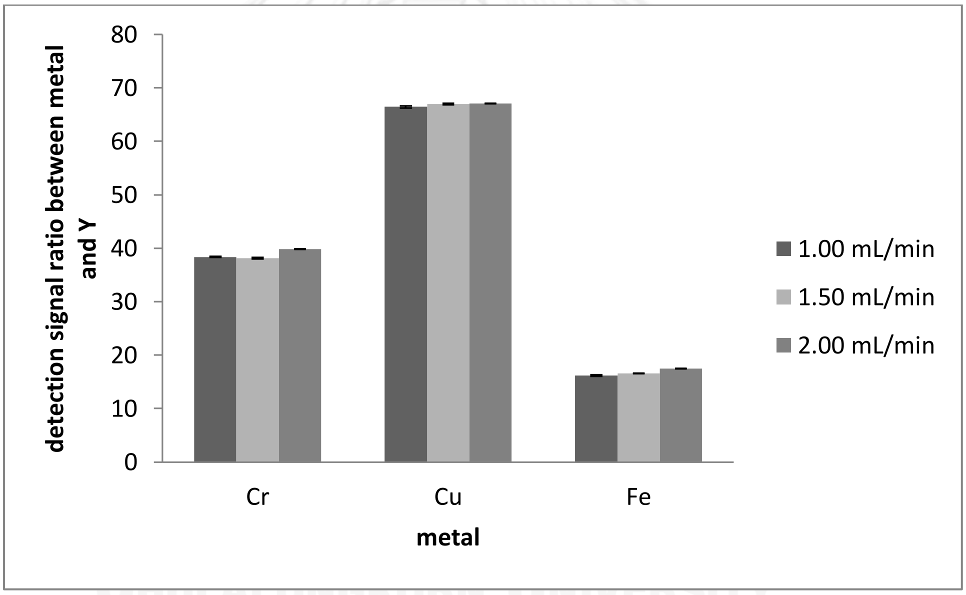


Figure 4.11 The signal ratio of metal in 1.00 µg g^{-1} multi-element oil solution and yttrium observed at different introduction flow rate.

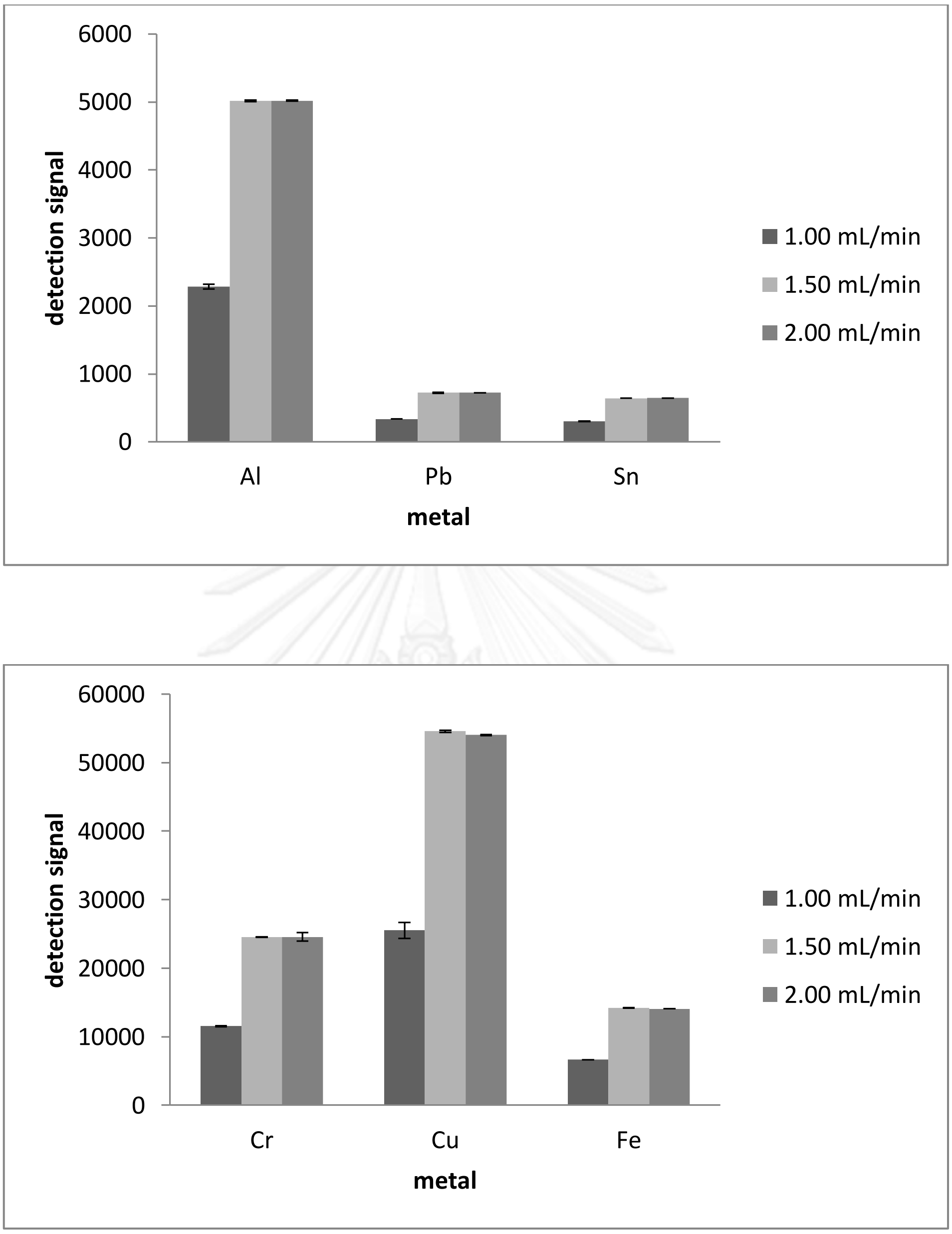
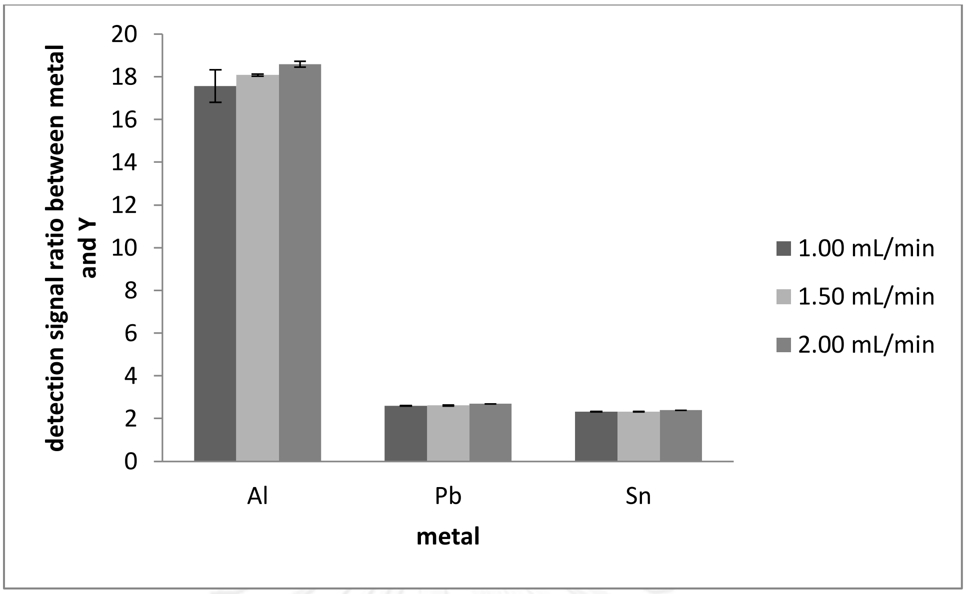


Figure 4.12 The signal of 5.00 µg g^{-1} multi-element oil solution observed at different introduction flow rate.



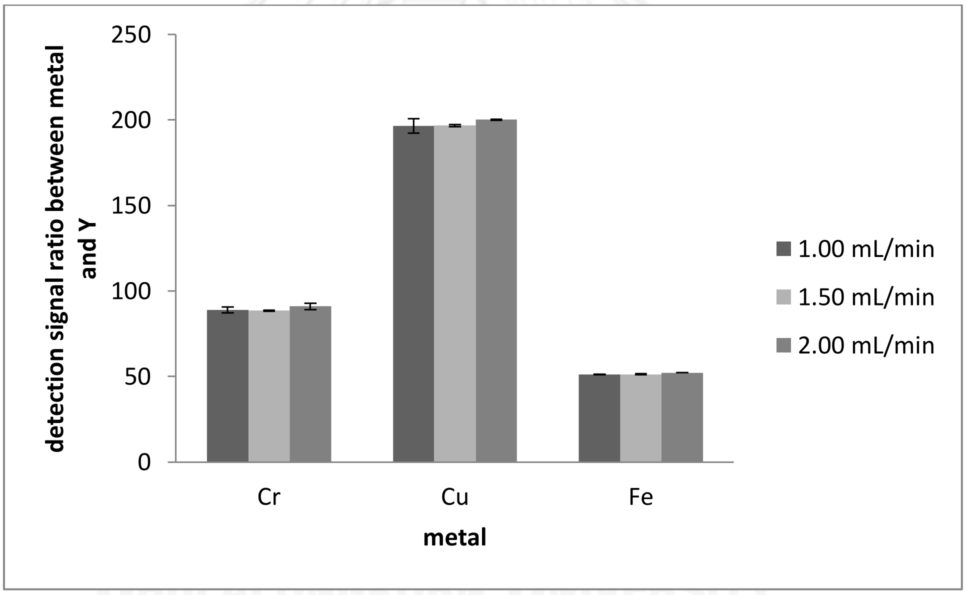


Figure 4.13 The signal ratio of metal in 5.00 µg g^{-1} multi-element oil solution and yttrium observed at different introduction flow rate.

The metals signal increased after increasing flow rate; on the contrary, all signals presented as ratio between metals and yttrium were not significantly different at the 95% confidential level despite the flow rate change level. It indicated that the internal standard addition can successfully improve analytical results accuracy.

The results observed at the solution introduction flow rate of 1.50 and 2.00 mL min^{-1} were not significantly different at the 95% confidential level. With a constant nebulization gas flow, the nebulization efficiency was limited. As the result, although the solution introduction flow rate was increased, the detection signal remained unchanged because the increasing amount of sample per time was not nebulized and passed into the plasma but drained from the spray chamber instead.

The flow rate of 1.50 mL min^{-1} was chosen due to the lower backpressure, despite a longer analysis time and lower sample throughput compared to the flow rate of 2.00 mL min^{-1}. In addition, it would extend the life time of the 2-channel syringe pump.

The solution introduction flow rate of 1.50 mL min^{-1} was employed in further experiments. In Table 4.18, the timing and sequence of system operation at this flow rate are given.

Table 4.18 The timing and sequence of system operation at flow rate of 1.50 mL min^{-1}

Number of step	Step	Duration (s)
1	Sample and solution loading	130
2	Sample flushing	40
3	Analysis	60
4	Cleaning	50

The sample throughput was 14 samples per hour.

4.2.5 Method validation

After the suitable conditions of automatic system for metals determination in oil by ICP-OES were obtained, the linear range of the method was observed. The linear range of the method is shown in Table 4.19.

Table 4.19 Linear range of the method for determination of metals in oil samples by ICP-OES observed at different wavelength

Metals-analytical wavelength (nm)	**Linear range ($\mu g\ g^{-1}$)**
Al-308.2	0.70-10.00
Cr-283.5	0.30-10.00
Cr-357.8	0.70-10.00
Cu-324.7	0.30-10.00
Fe-259.9	0.40-10.00
Pb-280.1	3.60-10.00
Pb-283.3	2.10-10.00
Sn-242.9	5.90-10.00

The method was validated by demonstrating the performance related to the precision of the analysis by observing the deviation in the analysis results for calibration curve construction, presented in term of %RSD of slope of linear equations of calibration curves obtained from intraday and interday analysis. LOD and LOQ were also determined. The results showed that this method produced results with good precision, as summarized in Table 4.20.

Table 4.20 Precision, LOD, and LOQ of the method for determination of metals in oil samples by ICP-OES coupled to the automatic internal standard addition system

Metals-analytical wavelength (nm)	RSD of slope (%)		LOD[c] ($\mu g\ g^{-1}$)	LOQ[d] ($\mu g\ g^{-1}$)
	Intraday[a]	Interday[b]		
Al-308.2	4.51	6.51	0.42	0.66
Cr-283.5	3.42	10.90	0.24	0.30
Cr-357.8	2.41	3.79	0.52	0.64
Cu-324.7	2.87	7.25	0.22	0.28
Fe-259.9	4.88	3.30	0.26	0.33
Pb-280.1	10.69	24.53	3.20	3.55
Pb-283.3	5.38	10.92	1.89	2.08
Sn-242.9	5.71	12.68	2.71	5.81

[a] n = 3

[b] n = 7 within 10 days

[c] LOD = the concentration that gave the signal equal to the summation of blank signal average and three times of blank signal SD

[d] LOQ = the concentration that gave the signal equal to the summation of blank signal average and ten times of blank signal SD

Moreover, the results from the automatic system were compared with the results obtained from direct injection of standard oil solutions, prepared by manually adding the internal standard, to ICP-OES via the instrument peristaltic pump (Table 4.21).

Table 4.21 Precision of the internal standard calibration obtained by the direct injection of oil standards manually mixed with yttrium

Metals-analytical wavelength (nm)	**RSD of slope[a] (%)**
Al-308.2	5.41
Cr-283.5	10.24
Cr-357.8	5.23
Cu-324.7	9.23
Fe-259.9	4.37
Pb-280.1	12.43
Pb-283.3	6.21
Sn-242.9	6.84

[a] n = 3

The results showed that the performance of both methods was significantly different at the 95% confidential level. The automatic system provided calibration results with lower %RSD or higher precision than that of the other method. It confirmed that the solution introduction to ICP-OES performed by a 2-channel syringe pump provided the stability of solution flow than that performed by a peristaltic pump. In the analysis of oil samples, moreover, the step of standard and sample preparation was probably not facile so it could cause error. Besides, using the automatic system is less laborious.

4.2.6 Analysis of oil samples

The method for determination of metals by the proposed automatic system coupled to ICP-OES was applied to the analysis of oil samples (crane engine used oil and car engine used oil) using spiked method. The results presented as %recovery are shown in Table 4.22. The recoveries were calculated obeyed Equation 1.

Table 4.22 Determination of Al, Cr, Cu, Fe, Pb and Sn in oil samples by internal standard method via the automatic system

Sample	Metals-analytical wavelength (nm)	Added ($\mu g\ g^{-1}$)	Found[a] ($\mu g\ g^{-1}$)	RSD [a] (%)	Recovery [a] (%)
Crane engine used oil 1	Al-308.2	-	n.d.	-	-
		3	3.02 ±0.02	0.69	100.49
	Cr-357.8	-	n.d.	-	-
		3	3.12 ± 0.17	5.31	104.03
	Cu-324.7	-	1.05 ± 0.24	22.24	-
		3	4.02 ± 0.05	1.12	98.58
	Fe-259.9	-	0.75 ± 0.10	12.93	-
		3	3.52 ± 0.04	1.20	91.98
	Pb-283.3	-	n.d.	-	-
		3	3.05 ± 0.04	1.23	100.70
	Sn-242.9	-	6.12 ± 0.13	2.12	-
		3	9.16 ± 0.03	0.33	101.33
Crane engine used oil 2	Al-308.2	-	n.d.	-	-
		3	2.97 ± 0.06	1.93	99.16
	Cr-357.8	-	n.d.	-	-
		3	3.02 ± 0.06	2.05	100.51
	Cu-324.7	-	2.21 ± 0.03	1.33	-
		3	5.03 ± 0.06	1.25	92.79
	Fe-259.9	-	1.25 ± 0.03	2.00	-
		3	3.94 ± 0.06	1.64	89.46
	Pb-283.3	-	n.d.	-	-
		3	3.14 ± 0.07	2.14	104.74
	Sn-242.9	-	6.68 ± 0.06	0.89	-
		3	9.73 ± 0.02	0.21	101.67

Table 4.22 Determination of Al, Cr, Cu, Fe, Pb and Sn in oil samples by internal standard method via the automatic system (cont.)

Sample	Metals-analytical wavelength (nm)	Added (µg g^{-1})	Found^{a} (µg g^{-1})	RSD ^{a} (%)	Recovery ^{a} (%)
Car engine used oil	Al-308.2	-	n.d.	-	-
		3	2.93 ± 0.08	1.32	97.78
	Cr-357.8	-	1.65 ± 0.04	2.42	-
		3	4.67 ± 0.04	0.86	100.67
	Cu-324.7	-	n.d.	-	-
		3	3.00 ± 0.02	0.66	100.00
	Fe-259.9	-	1.54 ± 0.04	2.60	-
		3	4.50 ± 0.06	0.89	98.67
	Pb-283.3	-	n.d.	-	-
		3	3.10 ± 0.07	2.26	103.33
	Sn-242.9	-	5.85 ± 0.03	0.51	-
		3	8.74 ± 0.03	0.34	96.33

^{a}mean ± SD (n=3)

The recoveries of Al, Cr, Cu, Fe, Pb, and Sn from samples spiked with Al, Cr, Cu, Fe, Pb, and Sn standard were in the range of 89.46–104.74 %, demonstrating that the method could be applied for the determination of Al, Cr, Cu, Fe, Pb, and Sn in oil samples with acceptable accuracy, in respect to the criteria in Table 4.7.

Moreover, the results collected from the automatic system were calculated by using external calibration method and the recoveries observed were shown in following table.

Table 4.23 Determination of Al, Cr, Cu, Fe, Pb and Sn in oil samples by external standard method via the automatic system

Sample	Metals-analytical wavelength (nm)	Added (μg g^{-1})	Found[a] (μg g^{-1})	RSD[a] (%)	Recovery[a] (%)
Crane engine used oil 1	Al-308.2	-	n.d.	-	-
		3	3.03 ±0.04	1.32	101.18
	Cr-357.8	-	n.d.	-	-
		3	3.15 ± 0.18	5.71	104.90
	Cu-324.7	-	0.97 ± 0.25	25.77	-
		3	4.11 ± 0.06	1.46	104.56
	Fe-259.9	-	0.64 ± 0.10	15.63	-
		3	3.57 ± 0.04	1.12	97.74
	Pb-283.3	-	n.d.	-	-
		3	3.45 ± 0.49	14.20	115.07
	Sn-242.9	-	6.49 ± 0.84	12.94	-
		3	9.56 ± 0.04	0.42	102.76
Crane engine used oil 2	Al-308.2	-	n.d.	-	-
		3	3.09 ± 0.09	2.91	102.92
	Cr-357.8	-	n.d.	-	-
		3	2.92 ± 0.11	3.77	97.37
	Cu-324.7	-	2.10 ± 0.13	6.19	-
		3	5.13 ± 0.09	1.75	102.86
	Fe-259.9	-	1.50 ± 0.04	2.67	-
		3	4.49 ± 0.08	1.78	99.75
	Pb-283.3	-	n.d.	-	-
		3	3.20 ± 0.47	14.69	106.71
	Sn-242.9	-	6.69 ± 0.56	8.37	-
		3	9.84 ± 0.12	1.22	104.90

Table 4.23 Determination of Al, Cr, Cu, Fe, Pb and Sn in oil samples by external standard method via the automatic system (cont.)

Sample	Metals-analytical wavelength (nm)	Added ($\mu g\ g^{-1}$)	Found^{a} ($\mu g\ g^{-1}$)	RSD^{a} (%)	Recovery^{a} (%)
Car engine used oil	Al-308.2	-	n.d.	-	-
		3	2.87 ± 0.68	23.69	95.71
	Cr-357.8	-	1.85 ± 0.44	23.78	-
		3	4.87 ± 0.32	6.57	100.62
	Cu-324.7	-	n.d.	-	-
		3	2.89 ± 0.12	4.15	96.30
	Fe-259.9	-	1.61 ± 0.20	12.42	-
		3	4.73 ± 0.26	5.50	103.95
	Pb-283.3	-	n.d.	-	-
		3	3.08 ± 0.17	5.52	102.82
	Sn-242.9	-	5.79 ± 0.53	9.15	-
		3	8.91 ± 0.13	1.46	104.15

^{a}mean ± SD (n=3)

The recoveries of the proposed method were compared to those of the external standard method via the automatic system in Figure 4.14-4.16.

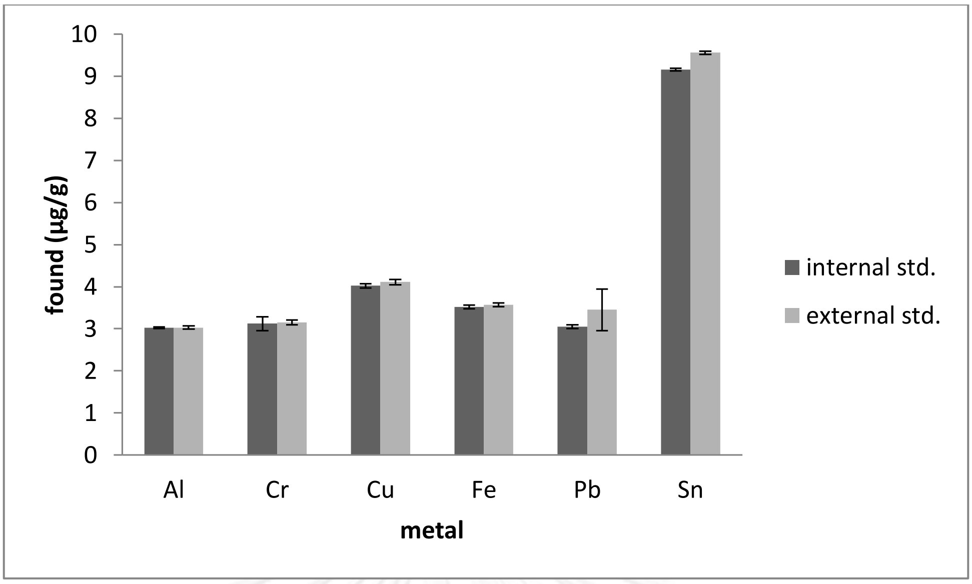


Figure 4.14 The found values of metals in crane engine used oil 1 spiked with 3 µg g^{-1} observed by using the internal standard method and the external standard method via the automatic system.

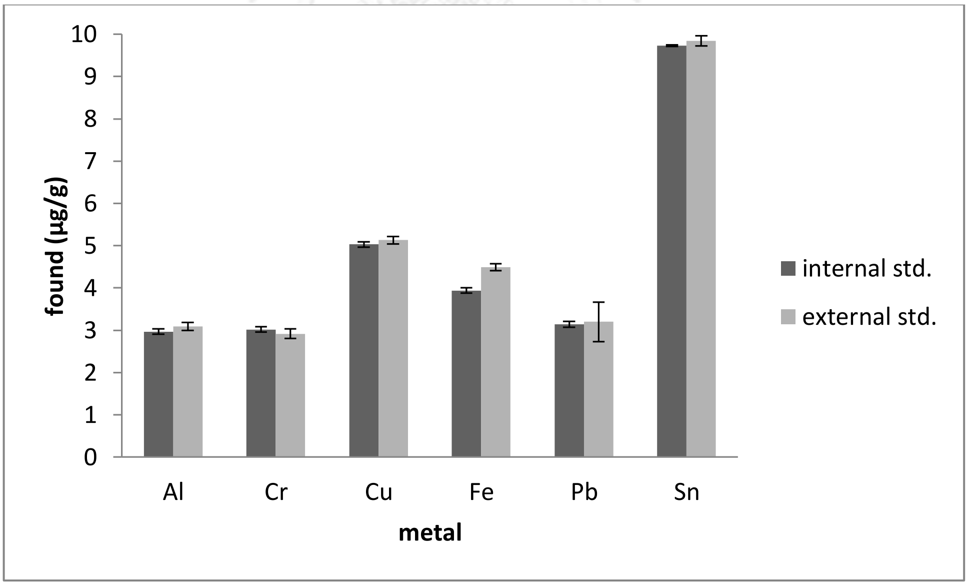


Figure 4.15 The found values of metals in crane engine used oil 2 spiked with 3 µg g^{-1} observed by using the internal standard method and the external standard method via the automatic system.

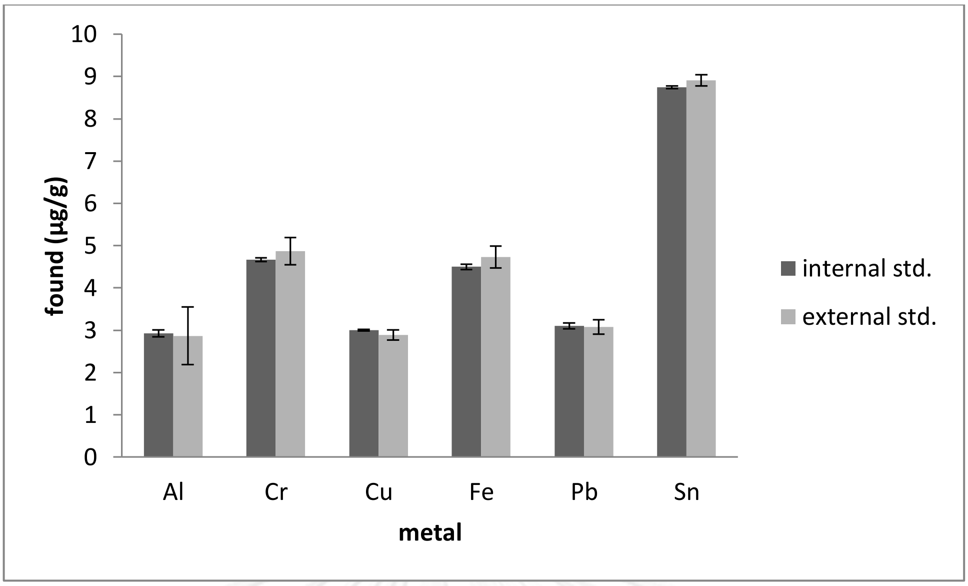


Figure 4.16 The found values of metals in car engine used oil spiked with 3 µg g^{-1} observed by using the internal standard method and the external standard method via the automatic system.

The results show that %RSD of the found values calculated by using the external standard method was higher than those from the internal standard method. It indicates the viscosity of oil sample affected the metal signal by altering the nebulization efficiency. In the analysis of crane engine oil samples, those effects were not demonstrated clearly due to the low viscosity of the samples. However, when car engine oil sample with high viscosity was analyzed, %RSD of results calculated from the external calibration standard method was high and the precision of the method was low. It confirmed that the internal standard was required in the determination of metal in oil samples.

In addition, the samples were analyzed by direct injection to ICP-OES via the instrument peristaltic pump after preparing by manually adding the internal standard into samples. The recoveries of metal analyzed by direct injection of oil standards and samples and calculated with the internal standard method were shown in the following table.

Table 4.24 Determination of Al, Cr, Cu, Fe, Pb and Sn in oil samples by the direct injection of oil standards manually mixed with yttrium

Sample	Metals-analytical wavelength (nm)	Added ($\mu g\ g^{-1}$)	Found[a] ($\mu g\ g^{-1}$)	RSD [a] (%)	Recovery [a] (%)
Crane engine used oil 1	Al-308.2	-	n.d.	-	-
		3	3.74 ±0.08	2.32	124.81
	Cr-357.8	-	n.d.	-	-
		3	3.75 ± 0.08	2.21	124.90
	Cu-324.7	-	1.50 ± 0.14	9.03	-
		3	5.06 ± 0.12	2.37	118.50
	Fe-259.9	-	0.78 ± 0.08	10.90	-
		3	4.37 ± 0.11	2.59	119.55
	Pb-283.3	-	n.d.	-	-
		3	3.89 ± 0.07	1.96	129.52
	Sn-242.9	-	4.23 ± 0.01	0.18	-
		3	8.07 ± 0.10	1.29	127.86
Crane engine used oil 2	Al-308.2	-	n.d.	-	-
		3	4.81 ± 0.32	6.54	160.46
	Cr-357.8	-	n.d.	-	-
		3	4.63 ± 0.25	5.49	154.45
	Cu-324.7	-	2.08 ± 0.06	2.71	-
		3	8.59 ± 0.52	6.09	216.89
	Fe-259.9	-	0.95 ± 0.02	2.28	-
		3	6.81 ± 0.48	7.09	195.17
	Pb-283.3	-	n.d.	-	-
		3	4.75 ± 0.27	5.61	159.70
	Sn-242.9	-	n.d.	-	-
		3	5.24 ± 0.32	6.10	176.22

Table 4.24 Determination of Al, Cr, Cu, Fe, Pb and Sn in oil samples direct by the direct injection of oil standards manually mixed with yttrium (cont.)

Sample	Metals-analytical wavelength (nm)	Added (µg g^{-1})	Found[a] (µg g^{-1})	RSD [a] (%)	Recovery [a] (%)
Car engine used oil	Al-308.2	-	n.d.	-	-
		3	2.01 ± 1.65	81.87	67.07
	Cr-357.8	-	n.d.	-	-
		3	1.75 ± 3.01	171.92	58.32
	Cu-324.7	-	n.d.	-	-
		3	2.21 ± 1.32	59.80	73.51
	Fe-259.9	-	0.82 ± 0.12	14.54	-
		3	2.52 ± 1.23	48.71	56.71
	Pb-283.3	-	n.d.	-	-
		3	2.33 ± 1.27	54.48	77.61
	Sn-242.9	-	n.d.	-	-
		3	1.96 ± 1.56	79.49	65.30

[a] mean ± SD (n=3)

The recoveries of direct injection method were compared to those of the automatic method in Figure 4.17-4.19.

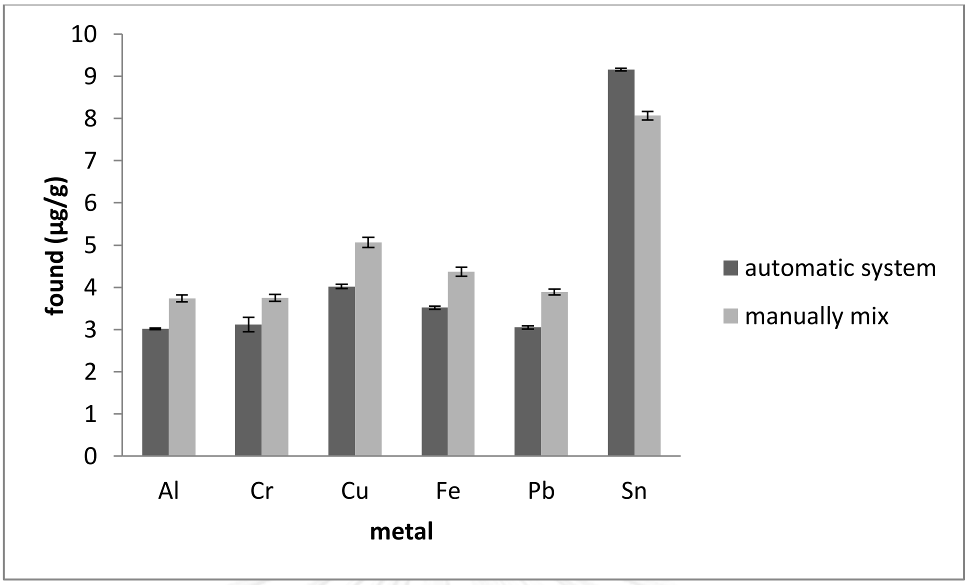


Figure 4.17 The found values of metal in crane engine used oil 1 spiked with 3 µg g^{-1} observed by using the automatic system and the direct injection of oil samples manually mixed with yttrium.

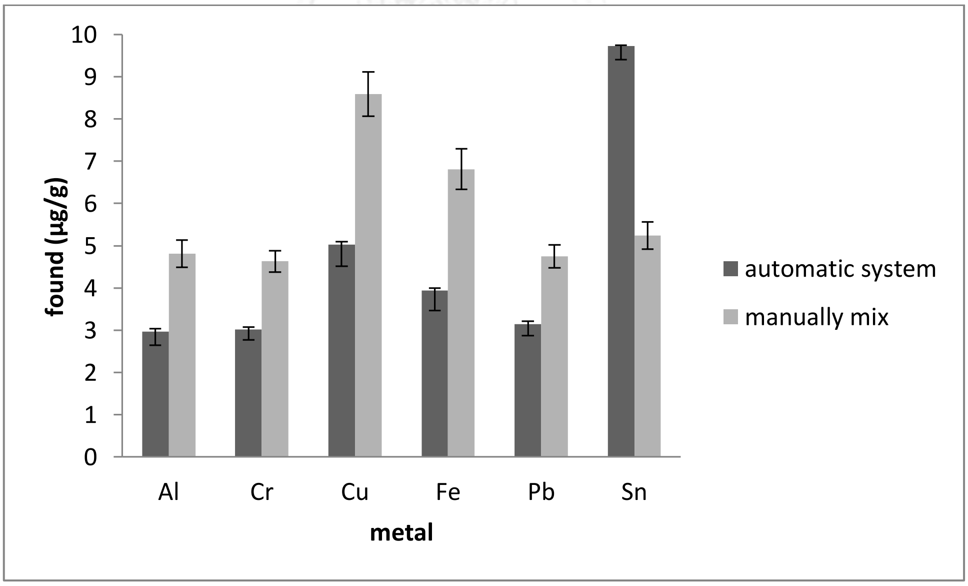


Figure 4.18 The found values of metal in crane engine used oil 2 spiked with 3 µg g^{-1} observed by using the automatic system and the direct injection of oil samples manually mixed with yttrium.

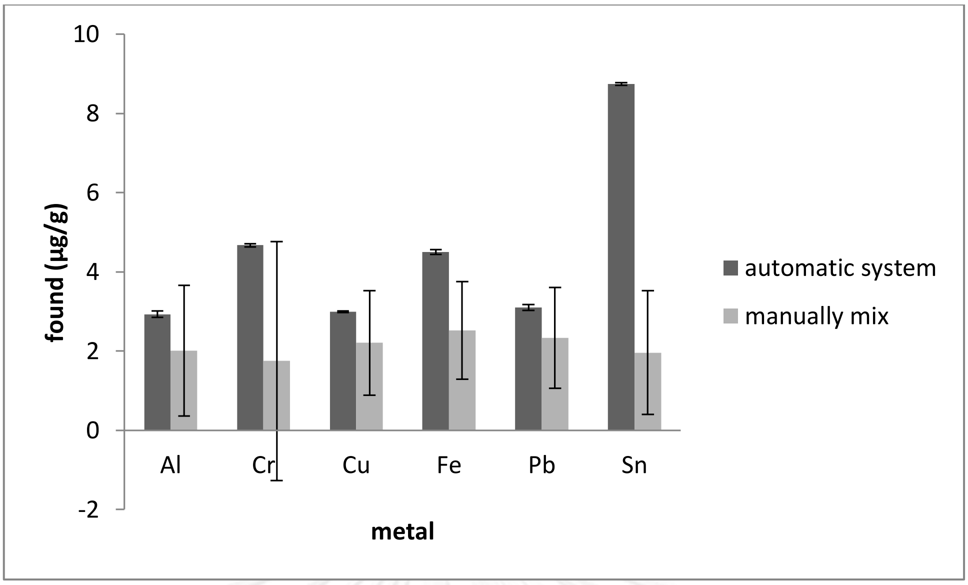


Figure 4.19 The found values of metal in car engine used oil spiked with 3 µg g^{-1} observed by using the automatic system and the direct injection of oil samples manually mixed with yttrium.

The results showed that %RSD of the found values obtained by direct injection of oil samples manually mixed with yttrium were higher than those from the proposed method. Furthermore, the recoveries were unacceptable following the criteria in Table 4.7. It indicated that the viscosity of oil sample affected the stability of solution introduction to ICP-OES by peristaltic pump operation. Moreover, manual sample or standard preparation was tedious and complicated and may lead to errors. It proved that the automatic system for internal standard addition could reduce the error from human and reduce the time consuming step.

The results of metal determination in crane engine oil samples obtained by the proposed method and the direct injection of manually prepared samples to ICP-OES via peristaltic pump showed acceptable recoveries and %RSD following the criteria in Table 4.7. However, the accuracy and the precision of results of metal determination in car engine oil sample by direct injection were unacceptable. It was explained by a high viscosity of the sample. When the ICP-OES peristaltic pump was operated to deliver the sample to ICP-OES, the pump could not be operated under the stability condition. In addition, the different viscosity between standard oil solution and car engine oil sample affected dramatically the recoveries calculated from calibration method. It suggested that using the syringe pump to introduce the sample of internal standard can overcome the errors from viscosity of sample. The automatic on-line internal standard addition system for determination of metals in oil was demonstrated that it provided the acceptable accuracies.

4.2.7 Analysis of certified reference material

The accuracy of the method was evaluated by analyzing Cr, Cu, Mn, and Ni in certified reference material (WM-11-NMS-5X-1, AccuStandard). The results are shown in Table 4.25.

Table 4.25 Determination of Al, Cr, Cu, Fe, Pb and Sn in certified reference material

Metals-analytical wavelength (nm)	Certified (μg g^{-1})	Found[a] (μg g^{-1})	RSD[a] (%)	Recovery[a] (%)
Al-308.2	50.00 ± 0.12	50.06 ± 0.79	1.56	100.11
Cr-357.8	50.00 ± 0.12	52.35 ± 2.56	4.90	104.70
Cu-324.7	50.00 ± 0.12	49.98 ± 1.48	2.95	99.95
Fe-259.9	50.00 ± 0.12	51.64 ± 0.51	0.99	103.28
Pb-283.3	50.00 ± 0.12	50.47 ± 3.26	6.47	100.94
Sn-242.9	50.00 ± 0.12	47.85 ± 1.44	3.01	95.71

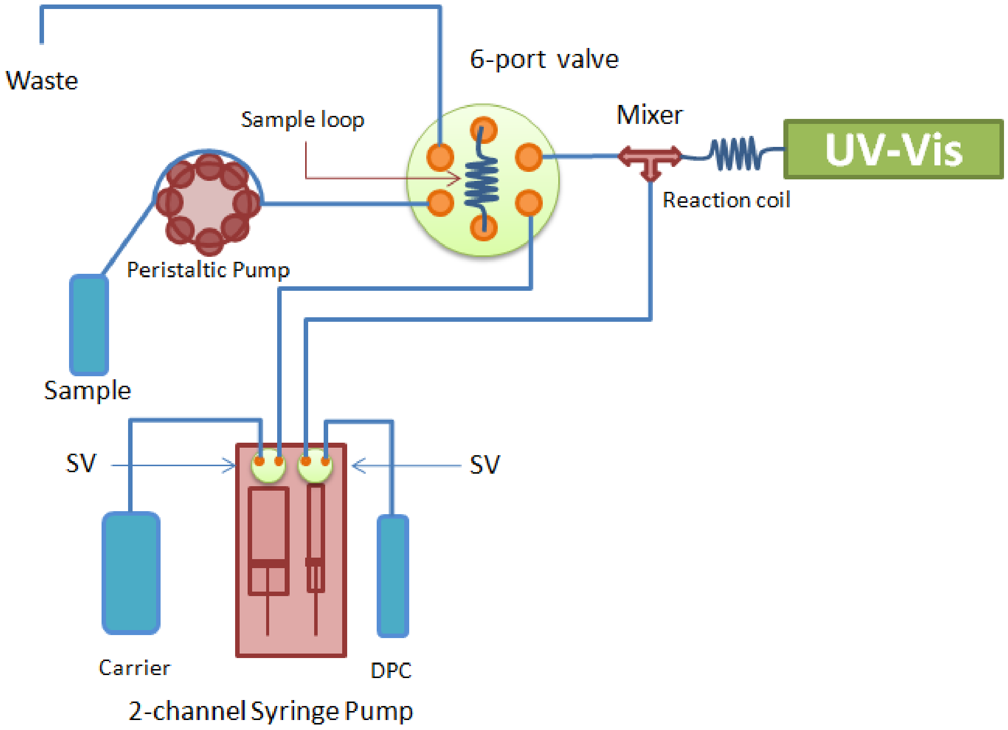
[a] mean ± SD (n=3)

The values obtained by the proposed method are not significantly different from the certified values at the 95% confidential level; therefore, the method could be applied for the determination of Al, Cr, Cu, Fe, Pb, and Sn in oil samples with acceptable accuracy.

4.3 Determination of Cr (VI) in aqueous solution by UV-Vis spectroscopy

4.3.1 Automatic system setup

Cr (VI) determination was based on the reaction of Cr (VI) with 1, 5-diphenyl carbazide (DPC). The automatic system was used for DPC addition to Cr (VI) sample solution and the mixture was further detected by UV-Vis spectrophotometer at 540 nm. Automatic system operating conditions are listed in Table 4.26.



Scheme 4.2 Automatic on-line analysis system with UV-Vis spectrophotometer (SV = solenoid valve and DPC = 1, 5-diphenylcarbazide).

Table 4.26 Automatic system operating conditions

Condition	Setting
Flow rate of solution loading into 2-channel syringe pump (1.00 mL and 250 µL) (mL min^{-1})	1.56
Peristaltic pump rate (for sample loading to sample loop) (rpm)	40

4.3.2 Effect of solution introduction flow rate

In the analysis, the time-based signal was observed as illustrated in Figure 4.20. The absorbance at peak maxima or signal peak height was used for quantification analysis.

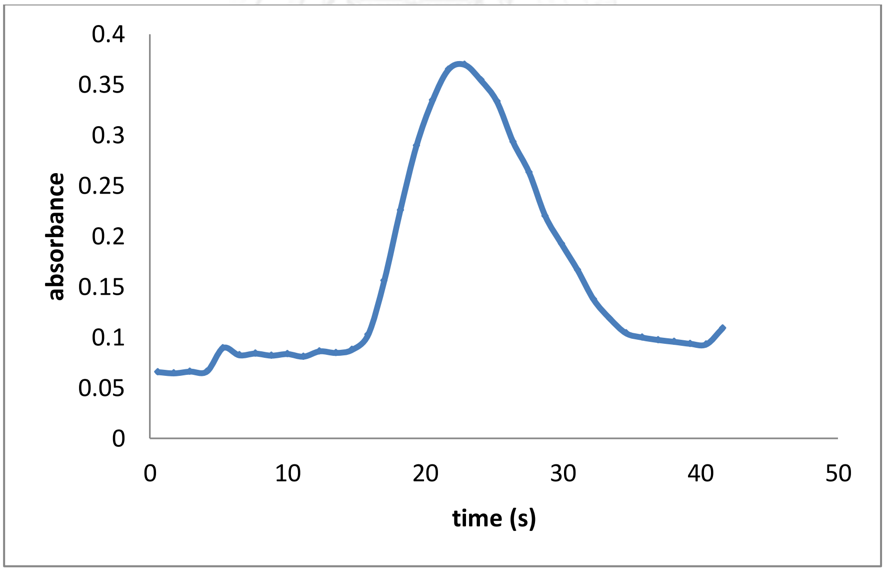


Figure 4.20 The signal of 1.00 mg L^{-1} Cr (VI) solution at introduction flow rate of 2.00 mL min^{-1}.

In general, a suitable solution introduction flow rate should provide a good sensitivity in signal detection and reasonable analysis time. The analysis time of different flow rate are reported in Table 4.27.

Moreover, the solution introduction flow rate may affect the sensitivity of detection. At low flow rate, the longitudinal diffusion may occur in the line, thus sensitivity was dropped because of the lowered concentration of mixture observed at detector. On the other hand, if the flow rate was too high, the detector may not detect the precise signal. In this study, the flow rate in a range from 1.00-2.00 mL min^{-1} was adopted and the results are shown in Figure 4.21.

Table 4.27 Analysis time of different introduction flow rate

Flow rate (mL min^{-1})	Analysis time (s)
1.00	85
1.50	43
2.00	33

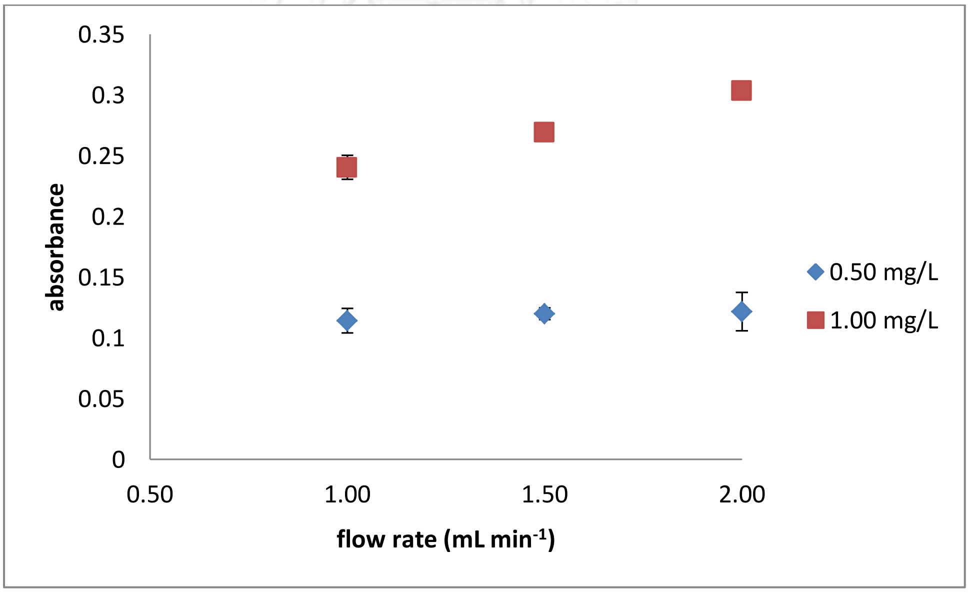


Figure 4.21 Detection signal observed at different flow rate.

The effect of flow rate on Cr (VI) detection is illustrated in the plot between peak heights versus flow rate. It is clearly observed that the signal of 1.00 mg L^{-1} solution increased when the flow rate was raised. However, the signal of 0.50 mg L^{-1} solution was not dramatically different as the flow rate changed, but the signal peak observed at flow rate of 2.00 mL min^{-1} had more symmetric shape, compared to the other flow rate (Figure 4.22). When the peak shape is symmetry, the integration of signal is likely to be correct. Then the flow rate at 2.00 mL min^{-1} was used for method validation.

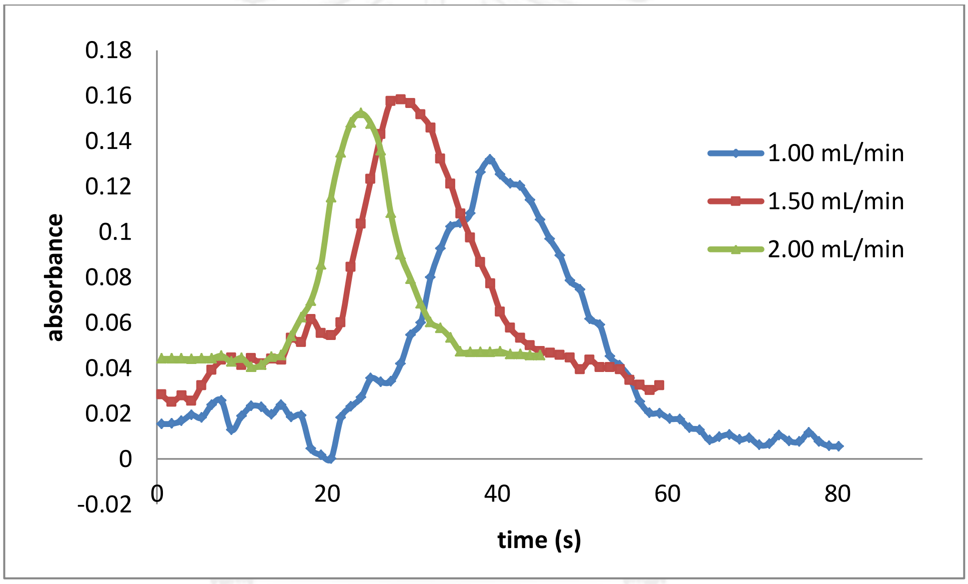


Figure 4.22 The shape of signal peak of 0.50 mg L^{-1} Cr (VI) solution observed at different flow rate.

4.3.3 Method validation

The peak height or the absorbance at peak maxima quantitatively increased with the amount of Cr (VI) that reacted with DPC, which followed Beer-Lambert's Law. In Figure 4.23, the linear relationship was obtained in the concentration range from 0.40-2.40 mg L^{-1} with the correlation coefficient (R^2) of higher than 0.99.

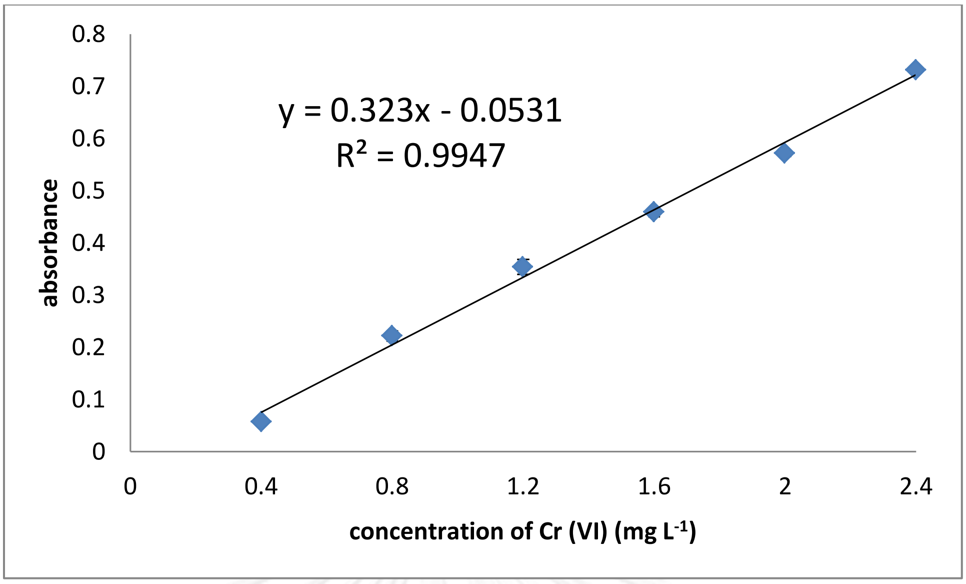


Figure 4.23 Calibration curve of Cr (VI) determined by UV-Vis spectrophotometer at 470 nm coupled to the proposed automatic system.

The validity of this method was determined by analyzing standard chromium (VI) solution at 3 concentration levels: 0.50, 1.00 and 1.40 mg L^{-1} as synthetic sample solutions. The accuracy and precision of the method were demonstrated as the percentage of recovery and %RSD, respectively. The recoveries were calculated obeyed Equation 2;

$$recovery\,(\%) = \frac{C_e}{C_t} \times 100 \qquad (2)$$

where C_e is the concentration calculated from calibration curve

C_t is the concentration from stock dilution

The LOD and LOQ were also determined.

Table 4.28 Accuracy, precision, LOD, and LOQ of the method for ultraviolet-visible spectrophotometer

Cr (VI) concentration (mg L^{-1})	Recovery[a] (%)	RSD[a] (%)	LOD[b] (mg L^{-1})	LOQ[c] (mg L^{-1})
0.50	96.79	3.95	0.24	0.33
1.00	94.34	1.89		
1.40	100.05	0.81		

[a] n = 3

[b] LOD = the concentration that gave the signal equal to the summation of blank signal average and three times of blank signal SD

[c] LOQ = the concentration that gave the signal equal to the summation of blank signal average and ten times of blank signal SD

According to the criteria in Table 4.7, the summarized results show that the method could produce results with acceptable accuracy and precision.

4.3.4 Analysis of blind samples

The method was applied to determine Cr (VI) in blind samples. The results are shown in Table 4.29.

Table 4.29 Analysis of Cr (VI) in blind samples

Blind sample	**Calculated concentration (mg L^{-1})**	**True concentration (mg L^{-1})**	**Recovery^{a} (%)**	**RSD^{a} (%)**
A	1.91 ± 0.02	2.00	95.33	1.09
B	0.98 ± 0.04	1.00	98.33	4.11
C	0.51 ± 0.03	0.50	102.00	5.19

[a] n = 3

According to the criteria in Table 4.7, this method could be employed to determine Cr (VI) in samples with acceptable accuracy and precision.

CHAPTER V
CONCLUSIONS

5.1 Conclusions

An automatic on-line internal standard addition system for determination of metals by inductively coupled plasma optical emission spectrometry (ICP-OES) was successfully developed and employed in the determination of metal in both aqueous phase and oil phase. The method produced results with acceptable accuracy and precision.

The operating conditions of the automatic system and ICP-OES affecting the determination of metals in aqueous and oil solutions were optimized. The operating conditions are shown in Table 5.1.

Table 5.1 The operating conditions of the automatic system and ICP-OES

Conditions	Setting	
	Aqueous solution	Oil solution
Peristaltic pump flow rate for sample loading to sample loop (rpm)	50	50
Flow rate of solution loading into 2-channel syringe pump (mL min^{-1})	6.41	6.41
Flow rate of solution introduction (mL min^{-1})	1.50	1.50
Flow rate of oxygen additional gas (L min^{-1})	n.a.	0.10

n.a. = not applicable

The sample throughput for the analysis of metal ions in aqueous and oil solution was 11 and 14 samples per hour, respectively. LOD and the recoveries of the determination of Cr, Cu, Mn, and Ni in aqueous samples were in the range of 2.5-

6.4 μg L^{-1} and 98.9-111.5 % for concentration lower than 10 μg L^{-1} level, 93.3-112.2 % for 10-100 μg L^{-1} level, and 85.9–108.0 % for the concentration higher than 100 μg L^{-1} level. LOD and the recoveries of the determination of Al, Cr, Cu, Fe, Pb, and Sn in oil sample were in the range of 0.22-2.71 μg g^{-1} and 89.46–104.74 %, respectively.

Moreover, the automatic system consisting of a 2-channel syringe pump equipped with a 6-port valve could also be applied to an on-line determination of chromium (VI) by coupling to ultraviolet-visible spectrophotometer. The reaction of Cr (VI) and DPC solution was adopted in the analysis. The operating conditions of the automatic system were optimized. The optimum solution introduction flow rate was 2.00 mL min^{-1}. The system provided an acceptable performance to measure chromium (VI). LOD of the determination of Cr (VI) was 0.24 mg L^{-1}.

5.2 Suggestions for future work

To reduce the analysis time, the single sample loop by using a 6-port valve could be replaced with double sample loops on an 8-port valve configuration. Furthermore, the automatic system consisted of a 2-channel syringe pump can also be applied to other solution addition and other method can be further developed using this system.

REFERENCES

[1] Naigaga, I., et al. Fish as bioindicators in aquatic environmental pollution assessment: A case study in Lake Victoria wetlands, Uganda. Physics and Chemistry of the Earth, Parts A/B/C 36(14-15) (2011): 918-928.

[2] Wagner, A. and Boman, J. Biomonitoring of trace elements in muscle and liver tissue of freshwater fish. Spectrochimica Acta Part B: Atomic Spectroscopy 58(12) (2003): 2215-2226.

[3] Zhang, Z., Wang, Z., Li, Q., Zou, H., and Shi, Y. Determination of trace heavy metals in environmental and biological samples by solution cathode glow discharge-atomic emission spectrometry and addition of ionic surfactants for improved sensitivity. Talanta 119 (2014): 613-9.

[4] Olesik, J.W. Elemental Analysis Using: An Evaluation and Assessment of Remaining Problems. Analytical Chemistry 63 (1991): 12A-17A.

[5] Hou, X. and Jones, B.T. Inductively Coupled Plasma/Optical Emission Spectrometry. Encyclopedia of Analytical Chemistry (2000): 9468-9485.

[6] Scott, R.H., Fassel, V.A., Kniseley, R.N., and Nixon, D.E. Inductively Coupled Plasma-Optical Emission Analytical Spectrometry: A Compact Facility for Trace Analysis of Solutions. Analytical Chemistry 46 (1974): 75-80.

[7] Aucélio, R.Q., de Souza, R.M., de Campos, R.C., Miekeley, N., and da Silveira, C.L.P. The determination of trace metals in lubricating oils by atomic spectrometry. Spectrochimica Acta Part B: Atomic Spectroscopy 62(9) (2007): 952-961.

[8] Bian, Q.Z., Jacob, P., Berndt, H., and Niemax, K. Online flow digestion of biological and environmental samples for inductively coupled plasma–optical emission spectroscopy (ICP–OES). Analytica Chimica Acta 538(1-2) (2005): 323-329.

[9] Horstkotte, B., Ledesma, E., Duarte, C.M., and Cerda, V. Improving Pressure Robustness, Reliability, and Versatility of Solenoid-Pump Flow Systems Using a Miniature Economic Control Unit Including TwoSimple Pressure Pulse Mathematical Models. Anal Chem 82: 6983-6990.

[10] Harris, D.C. Quantitative Chemical Analysis. 6th ed. New York: W.H. Freeman & Company, 2003.

[11] Krejcova, A., Cernohorsky, T., and Meixner, D. Elemental analysis of instant soups and seasoning mixtures by ICP–OES. Food Chemistry 105(1) (2007): 242-247.

[12] Toxic Substances: International heavy metals, POPs protocols finalized. Environmental Science & Technology 32(7) (1998): 169A-169A.

[13] The maximum permitted levels of some heavy metals in wastewater discharged from industries Department, P.C., Editor. 1996.

[14] Toms, L.A. Methods, Automation and Benefits. VA: Virginia Beach, 1998.

[15] Roylance, B.J. and Hunt, T.M. The Wear Debris Analysis Handbook. Oxford: Coxmoor Publishing Company, 1999.

[16] Hunt, T.M. Oil debris monitoring. in Rao, B.K.N. (ed.)Handbook of Condition Monitoring pp. 325-339. Oxford: Elseveir Science Ltd., 1996.

[17] Vähäoja, P., Välimäki, I., Roppola, K., Kuokkanen, T., and Lahdelma, S. Wear Metal Analysis of Oils. Critical Reviews in Analytical Chemistry 38(2) (2008): 67-83.

[18] Burrows, J.A., Heerdt, J.C., and Willis, J.B. Determination of wear metals in used lubricating oils by atomic absorption spectrometry. Anal. Chem 37 (1966): 579-582.

[19] Jansen, E.B.M., Knipscheer, J.H., and Nagtegaal, M. Rapid and accurate element determination in lubricating oils using inductively coupled plasma optical emission spectrometry. J. Anal. At. Spectrom 7 (1992): 127-130.

[20] Skoog, D.A. and Leary, J.J. Principles of Insrumental Analysis. Orlando, FL: Harcourt Brace & Company, 1992.

[21] Svehla, G. Vogel's qualitative inorganic analysis, ed. 7th. Singapore: Longman Singapore Publishers (Pte) Ltd., 1997.

[22] THIRUMALAI NIVAS, B., DAVID, A.S., SHIAU, B.J., and HARWELL, J.H. SURFACTANT ENHANCED REMEDIATION OF SUBSURFACE CHROMIUM CONTAMINATION. Wat. Res 30(3) (1996): 511-520.

[23] Themelis, D.G., Karastogianni, S.C., and Tzanavaras, P.D. Selective determination of cyanides by gas diffusion-stopped flow-sequential injection analysis and an on-line standard addition approach. Anal Chim Acta 632(1) (2009): 93-100.

[24] Tu, Q., Wang, T., and Welch, C.J. High-throughput metal screening in pharmaceutical samples by ICP-MS with automated flow injection using a modified HPLC configuration. J Pharm Biomed Anal 51(1) (2010): 90-5.

[25] Beck, N.G., Franks, R.P., and Bruland, K.W. Analysis for Cd, Cu, Ni, Zn, and Mn in Esturine water by ICP-MS coupled with an automated flow injection system. Analytica Chimica Acta 455 (2002): 11-22.

[26] Jitmanee, K., Teshima, N., Sakai, T., and Grudpan, K. DRC ICP-MS Coupled with Automated Flow Injection System with Anion Exchange Minicolumns for Determination of Selenium Compounds in Water Samples. Talanta 73(352-357) (2007).

[27] Rocha, A.A., Miekeley, N., Bezerra, M.C.M., and Küchler, I.L. An automated system for preconcentration/matrix-removal followed by ICP-MS determination of organic phosphorus in oil production water. Microchemical Journal 78(1) (2004): 65-70.

[28] Pinto, P.C.A.G., Saraiva, M.L.M.F.S., and Lima, J.L.F.C. A flow sampling strategy for the analysis of oil samples without pre-treatment in a sequential injection analysis system. Analytica Chimica Acta 555(2) (2006): 377-383.

[29] Mark, R.L. Validation and qualification in analytical laboratories. Illinois: Interpharm Press, 1999.

APPENDICES

Appendix 1

The Photographs of Automatic System

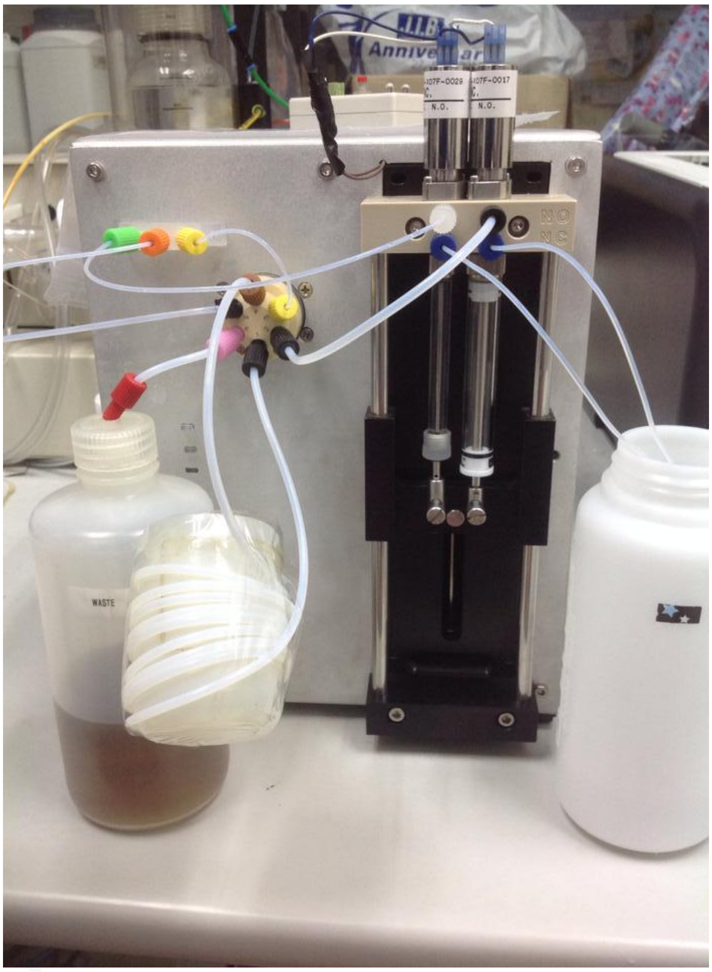


Figure A1-1 The automatic on-line internal standard addition system: the 2-channel syringe pump and 6-port valve equipped with sample loop.

Figure A1-2 The automatic on-line internal standard addition system: the mixture introduction line to ICP-OES and the line for solution loading to sample loop in top view.

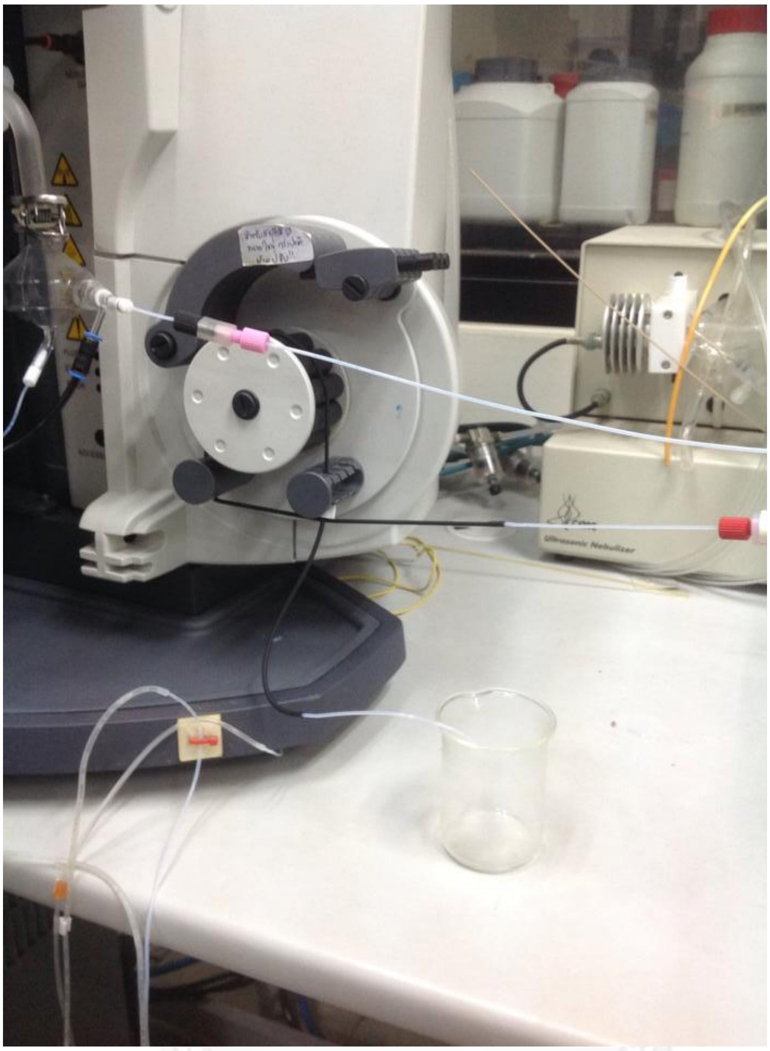


Figure A1-3 The automatic on-line internal standard addition system: the mixture introduction line to ICP-OES and the line for solution loading to sample loop in side view.

Appendix 2

Tables of Spiked Water Sample Recoveries

Table A2-1 Determination of Cr, Cu, Mn, and Ni in drinking water by external standard method via automatic system

Added ($\mu g\ L^{-1}$)	Metals-analytical wavelength (nm)					
	Cr-283.5			Cu-224.7		
	Found[a] ($\mu g\ L^{-1}$)	RSD[a] (%)	Recovery[a] (%)	Found[a] ($\mu g\ L^{-1}$)	RSD[a] (%)	Recovery[a] (%)
-	n.d.	-	-	n.d.	-	-
3	n.d.	-	-	n.d.	-	-
5	n.d.	-	-	n.d.	-	-
9	n.d.	-	-	n.d.	-	-
30	32.0 ± 1.0	3.1	106.7	n.d.	-	-
50	54.1 ± 2.8	5.2	108.2	n.d.	-	-
90	96.8 ± 1.9	2.0	107.6	n.d.	-	-
300	295.4 ± 1.5	0.5	98.5	294.5 ± 3.0	1.0	98.2
500	498.9 ± 1.1	0.2	99.8	497.8 ± 0.7	0.1	99.6
900	891.5 ± 5.9	0.7	99.1	887.1 ± 6.4	0.7	98.6
3000	3186.9 ± 106.5	3.4	106.2	2988.3 ± 97.3	3.2	99.6
5000	5068.5 ± 63.2	1.1	101.4	5109.8 ± 14.1	0.3	102.1
9000	8978.6 ± 20.4	0.2	99.8	9039.5 ± 53.3	0.6	100.4

Table A2-1 Determination of Cr, Cu, Mn, and Ni in drinking water by external standard method via automatic system (cont.)

Added (µg L^{-1})	**Metals-analytical wavelength (nm)**					
	Mn-257.6			**Ni-352.4**		
	Found^{a} (µg L^{-1})	RSD^{a} (%)	Recovery^{a} (%)	Found^{a} (µg L^{-1})	RSD^{a} (%)	Recovery^{a} (%)
-	n.d.	-	-	n.d.	-	-
3	n.d.	-	-	n.d.	-	-
5	n.d.	-	-	n.d.	-	-
9	8.8 ± 0.3	3.4	97.8	n.d.	-	-
30	31.7 ± 0.4	1.3	105.7	30.6 ± 0.7	2.3	102.0
50	52.4 ± 3.7	7.1	104.8	53.5 ± 1.4	2.6	107.0
90	94.8 ± 1.3	1.4	105.3	99.9 ± 9.94	9.9	111.0
300	287.6 ± 1.2	0.4	95.9	318.9 ± 1.5	0.5	106.3
500	485.2 ± 1.5	0.3	97.0	525.5 ± 2.9	0.6	105.1
900	869.6 ± 4.9	0.6	96.6	930.2 ± 12.0	1.3	103.4
3000	3203.8 ± 7.1	0.2	106.8	3049.9 ± 54.3	1.8	101.7
5000	4842.4 ± 28.1	0.6	96.8	5038.2 ± 24.0	0.5	100.8
9000	9091.8 ± 39.9	0.4	101.0	9033.8 ± 18.1	0.2	100.4

^{a}mean ± SD (n=3)

n.d. = non detectable

Table A2-2 Determination of Cr, Cu, Mn, and Ni in pool water by external standard method via automatic system

Added ($\mu g\ L^{-1}$)	Metals-analytical wavelength (nm)					
	Cr-283.5			Cu-224.7		
	Found[a] ($\mu g\ L^{-1}$)	RSD[a] (%)	Recovery[a] (%)	Found[a] ($\mu g\ L^{-1}$)	RSD[a] (%)	Recovery[a] (%)
-	n.d.	-	-	n.d.	-	-
3	n.d.	-	-	n.d.	-	-
5	n.d.	-	-	n.d.	-	-
9	n.d.	-	-	n.d.	-	-
30	32.1 ± 0.6	1.9	107.0	n.d.	-	-
50	51.4 ± 0.3	0.6	102.2	n.d.	-	-
90	94.2 ± 5.6	5.9	104.7	n.d.	-	-
300	284.2 ± 0.9	0.3	94.7	285.6 ± 0.8	0.3	95.2
500	477.8 ± 1.4	0.3	95.6	477.6 ± 1.7	0.4	95.5
900	856.3 ± 9.6	1.1	95.1	862.1 ± 2.1	0.2	95.8
3000	2940.0 ± 145.0	4.9	98.0	2847.6 ± 51.9	1.8	94.9
5000	5001.2 ± 121.0	2.4	100.0	5049.3 ± 38.2	0.8	101.0
9000	9093.6 ± 147.3	1.6	101.0	9300.2 ± 133.4	1.4	103.3

Table A2-2 Determination of Cr, Cu, Mn, and Ni in pool water by external standard method via automatic system (cont.)

Added ($\mu g\ L^{-1}$)	Metals-analytical wavelength (nm)					
	Mn-257.6			Ni-352.4		
	Found[a] ($\mu g\ L^{-1}$)	RSD[a] (%)	Recovery[a] (%)	Found[a] ($\mu g\ L^{-1}$)	RSD[a] (%)	Recovery[a] (%)
-	n.d.	-	-	n.d.	-	-
3	n.d.	-	-	n.d.	-	-
5	n.d.	-	-	n.d.	-	-
9	9.1 ± 0.5	5.5	101.1	n.d.	-	-
30	30.6 ± 2.3	7.5	102.0	30.6 ± 0.4	1.3	102.0
50	53.0 ± 2.4	4.5	106.0	56.3 ± 3.6	6.4	101.3
90	90.2 ± 7.2	8.0	100.2	87.5 ± 3.8	4.3	109.4
300	281.1 ± 1.2	0.4	93.7	312.4 ± 6.1	2.0	104.1
500	473.3 ± 1.2	0.3	94.7	510.5 ± 5.7	1.1	102.1
900	855.0 ± 7.4	0.9	95.0	903.5 ± 12.6	1.4	100.4
3000	3002.1 ± 55.8	1.9	100.1	2916.0 ± 172.1	5.9	97.2
5000	5065.9 ± 39.6	0.8	101.3	5002.6 ± 65.2	1.3	100.5
9000	9275.1 ± 139.0	1.5	103.1	8896.3 ± 156.3	1.8	98.8

[a] mean ± SD (n=3)

n.d. = non detectable

Table A2-3 Determination of Cr, Cu, Mn, and Ni in tap water by external standard method via automatic system

Added (μg L^{-1})	Metals-analytical wavelength (nm)					
	Cr-283.5			Cu-224.7		
	Found[a] (μg L^{-1})	RSD[a] (%)	Recovery[a] (%)	Found[a] (μg L^{-1})	RSD[a] (%)	Recovery[a] (%)
-	n.d.	-	-	n.d.	-	-
3	n.d.	-	-	n.d.	-	-
5	n.d.	-	-	n.d.	-	-
9	n.d.	-	-	n.d.	-	-
30	30.9 ± 1.5	4.9	101.1	n.d.	-	-
50	50.1 ± 1.9	3.8	100.6	n.d.	-	-
90	90.9 ± 4.3	4.7	100.9	n.d.	-	-
300	288.2 ± 1.0	0.4	96.1	281.7 ± 6.6	2.3	93.9
500	487.9± 2.0	0.4	97.6	480.9 ± 0.7	0.2	96.2
900	880.0 ± 3.0	0.3	97.8	865.8 ± 2.7	0.3	96.2
3000	2978.8 ± 47.1	1.6	97.1	3034.5 ± 93.7	3.1	101.2
5000	5010.2 ± 55.6	1.1	100.9	4620.6 ± 69.4	1.5	92.4
9000	8919.9 ± 194.1	2.2	99.8	9487.6 ± 58.6	0.6	105.4

Table A2-3 Determination of Cr, Cu, Mn, and Ni in tap water by external standard method via automatic system (cont.)

Added (µg L^{-1})	**Metals-analytical wavelength (nm)**					
	Mn-257.6			**Ni-352.4**		
	Found[a] (µg L^{-1})	**RSD[a] (%)**	**Recovery[a] (%)**	**Found[a] (µg L^{-1})**	**RSD[a] (%)**	**Recovery[a] (%)**
-	n.d.	-	-	n.d.	-	-
3	n.d.	-	-	n.d.	-	-
5	n.d.	-	-	n.d.	-	-
9	9.8 ± 0.7	7.1	108.9	n.d.	-	-
30	30.5 ± 2.6	8.5	101.7	32.0 ± 4.3	13.4	106.7
50	53.0 ± 3.0	5.7	106.0	53.4 ± 3.7	6.9	106.8
90	83.2 ± 4.2	5.0	104.0	94.5 ± 4.9	5.2	105.0
300	282.4 ± 1.4	0.5	94.1	321.4 ± 2.9	0.9	107.1
500	478.0 ± 1.7	0.3	95.6	524.8 ± 3.5	0.7	105.0
900	865.6 ± 2.2	0.3	96.2	924.2 ± 4.0	0.4	102.7
3000	3104.2 ± 152.2	4.9	103.5	3104.3 ± 99.2	3.2	103.5
5000	5193.8 ± 48.9	0.9	103.9	5110.5 ± 119.1	2.3	102.2
9000	8697.0 ± 218.0	2.5	96.6	9084.4 ± 61.2	0.7	100.9

[a] mean ± SD (n=3)

n.d. = non detectable

Table A2-4 Determination of Cr, Cu, Mn, and Ni in river water by external standard method via automatic system

Added (µg L^{-1})	Metals-analytical wavelength (nm)					
	Cr-283.5			Cu-224.7		
	Found[a] (µg L^{-1})	RSD[a] (%)	Recovery[a] (%)	Found[a] (µg L^{-1})	RSD[a] (%)	Recovery[a] (%)
-	n.d.	-	-	n.d.	-	-
3	n.d.	-	-	n.d.	-	-
5	n.d.	-	-	n.d.	-	-
9	n.d.	-	-	n.d.	-	-
30	33.1 ± 2.3	7.0	110.3	n.d.	-	-
50	51.4 ± 1.5	2.9	102.8	n.d.	-	-
90	91.6 ± 2.6	2.8	101.8	n.d.	-	-
300	288.0 ± 0.7	0.3	96.0	286.4 ± 1.7	0.6	95.5
500	478.1 ± 1.8	0.4	95.6	477.9 ± 2.3	0.5	95.6
900	860.8 ± 2.0	0.2	95.7	865.4 ± 2.2	0.3	96.2
3000	3108.3 ± 55.1	1.8	103.6	3069.1 ± 53.3	1.7	102.3
5000	5189.0 ± 66.4	1.3	103.8	5042.4 ± 45.4	0.9	100.8
9000	9032.7 ± 19.8	0.2	100.4	8897.3 ± 48.4	0.5	98.9

Table A2-4 Determination of Cr, Cu, Mn, and Ni in river water by external standard method via automatic system (cont.)

Added ($\mu g\ L^{-1}$)	Metals-analytical wavelength (nm)					
	Mn-257.6			Ni-352.4		
	Found[a] ($\mu g\ L^{-1}$)	RSD[a] (%)	Recovery[a] (%)	Found[a] ($\mu g\ L^{-1}$)	RSD[a] (%)	Recovery[a] (%)
-	n.d.	-	-	n.d.	-	-
3	n.d.	-	-	n.d.	-	-
5	n.d.	-	-	n.d.	-	-
9	9.3 ± 0.5	5.4	103.3	n.d.	-	-
30	29.4 ± 1.5	5.1	98.0	34.0 ± 1.7	5.0	113.3
50	54.1 ± 1.0	1.8	108.2	53.0 ± 3.1	5.8	106.0
90	95.8 ± 1.1	1.1	106.4	94.6 ± 2.4	2.5	105.1
300	281.2 ± 0.5	0.2	93.8	313.6 ± 1.8	0.6	104.5
500	468.3 ± 2.2	0.5	93.7	500.9 ± 3.7	0.7	100.2
900	850.9 ± 2.0	0.2	94.5	898.0 ± 2.5	0.3	99.8
3000	3201.6 ± 79.7	2.5	106.7	3164.3 ± 91.3	2.9	105.5
5000	4963.4 ± 109.4	2.2	99.3	4980.6 ± 122.6	2.5	99.6
9000	9374.4 ± 287.6	3.1	104.2	9038.0 ± 6.5	0.1	100.4

[a] mean ± SD (n=3)

n.d. = non detectable

Table A2-5 Determination of Cr, Cu, Mn, and Ni in wastewater by external standard method via automatic system

Added (μg L^{-1})	Metals-analytical wavelength (nm)					
	Cr-283.5			Cu-224.7		
	Found[a] (μg L^{-1})	RSD[a] (%)	Recovery[a] (%)	Found[a] (μg L^{-1})	RSD[a] (%)	Recovery[a] (%)
-	n.d.	-	-	n.d.	-	-
3	n.d.	-	-	n.d.	-	-
5	n.d.	-	-	n.d.	-	-
9	n.d.	-	-	n.d.	-	-
30	32.5 ± 3.6	11.1	108.3	n.d.	-	-
50	51.4 ± 1.5	2.9	102.8	n.d.	-	-
90	92.0 ± 1.6	1.7	102.2	n.d.	-	-
300	268.6 ± 3.8	1.4	89.5	270.0 ± 2.0	0.8	90.0
500	457.1 ± 13.6	3.0	91.4	452.3 ± 4.4	1.0	90.5
900	820.5 ± 2.5	0.3	91.2	811.3 ± 16.8	2.1	90.1
3000	3201.1 ± 52.6	1.6	106.7	2932.1 ± 50.6	1.7	97.7
5000	5244.1 ± 17.9	0.3	104.9	5112.3 ± 98.0	1.9	102.2
9000	8802.6 ± 50.3	0.6	97.8	9088.9 ± 36.8	0.4	101.0

Table A2-5 Determination of Cr, Cu, Mn, and Ni in wastewater by external standard method via automatic system (cont.)

Added (μg L^{-1})	Metals-analytical wavelength (nm)					
	Mn-257.6			Ni-352.4		
	Found^{a} (μg L^{-1})	RSD^{a} (%)	Recovery^{a} (%)	Found^{a} (μg L^{-1})	RSD^{a} (%)	Recovery^{a} (%)
-	n.d.	-	-	n.d.	-	-
3	n.d.	-	-	n.d.	-	-
5	n.d.	-	-	n.d.	-	-
9	10.1 ± 0.6	5.9	112.2	n.d.	-	-
30	31.8 ± 0.7	2.2	106.0	32.9 ± 1.8	5.5	109.7
50	48.2 ± 2.8	5.8	96.4	51.3 ± 3.3	6.4	102.6
90	86.3 ± 1.4	1.6	95.9	87.8 ± 2.6	3.0	97.5
300	258.3 ± 8.0	3.1	86.1	303.2 ± 4.7	1.5	101.1
500	438.4 ± 12.3	2.8	87.7	503.4 ± 31.9	6.3	100.7
900	790.1 ± 2.0	0.3	87.8	870.0 ± 3.3	0.4	96.7
3000	3100.6 ± 57.3	1.8	103.4	3033.4 ± 103.6	3.4	101.1
5000	4512.0 ± 193.5	4.3	90.2	5110.2 ± 277.6	5.4	102.2
9000	9300.0 ± 241.0	2.6	103.3	9261.1 ± 72.1	0.8	102.9

^{a}mean ± SD (n=3)

n.d. = non detectable

VITA

Mr. Pitcha Singhaphan was born on the seventh of October 1988 in Trat, Thailand. He has got the scholarship from the Development and Promotion of Science and Technology Talent Project (DPST) since 2009. He received his Bachelor's degree of Science from Chulalongkorn University in 2011 with first class honor. Then, he has continued the graduate study in the Department of Chemistry, Faculty of Science, Chulalongkorn University and has become a member of Environmental Analysis Research Unit. He finished his postgraduate study with the Master degree of Science 2014. His permanent address is 13/8 Chaimonkol Road, Bangphra, Mueang Trat District, Trat, 23000 and his E-mail is pitchasing@gmail.com.