CHAPTER 1

Introduction

1.1 **Ping river**

กษยนุด ปอ 1.1.1 General background

Ping river is the main water supply for Chiang Mai and it is also an upstream river which flows through many provinces of Thailand. The Ping river is one of the contributories and largest tributary of Chao Phraya river [Traichaiyaporn, 2008, Mae Ping river, 2008, Lebel, 2009, Reda, 2012]. Ping river, with length of approximately 600 kilometers, has its source from the Chiang Dao district in Chiang Mai Province (Figure 1.1). For over 700 years, the Ping river has been a main river and a major source of water for Chiang Mai people. Water is used in various activities, such as consumption, agriculture and irrigation [Mae Ping River, 2008, Lebel, 2009, Reda, 2012]. Over the last five decades (1960 - 2009) water and land in the Upper Ping has been transformed by enlargement and intensification of agriculture, industrial growth and tourism [Lebel, 2009]. As a result, the surface water quality is deteriorating due to anthropogenic activities, industrialization, farming activities, transportation, urbanization, animal and human excretions and domestic wastes [Traichaiyaporn, 2008]. Therefore, the water monitoring is necessary for assessment of water quality of the Ping river.

1.1.2 Water quality parameter for the Ping river

There are many parameters that indicating quality of water, which can be classified into 5 groups as shown in Table 1.1 [Water Reuse Center, 2014]. The determination of these parameters requires a lot of resources and takes long time. In practice some parameters are selected as water quality index to represent quality of water. The water quality index (WQI) was used to consider for surface water classification or the assessment of utilization and water pollution by using standard water quality parameters. The water quality assessment by using WQI is a simple practice, this enables the classification of adequate water quality. The determination of WQI requires a normalization step where each parameter is transformed into a 0-100 scale, where 100 demonstrates the high quality. And then, the next step is application of a weighting factor in concordance with the importance of the water quality parameter [Sánchez, 2007, Koçer, 2014]. The Ping river has been studied for some parameters that affect water quality. Quality of running water in some areas of Chiang Mai based on chemical criteria has been previously studied [Napattalung, 1997]. There are sixteen parameters to be determined. The data obtained were analyzed using statistical package, SPSSWIN to generate the Water Quality Index (WQI) for the classification of water quality. It was found that the five parameters, i.e. conductivity, dissolved oxygen, biochemical oxygen demand, ammonia and total phosphate could be used for constructing WQI equation that reflect quality of water. Moreover, in rainy season water has high turbidity due to soil erosion, which input large amounts of iron [Traichaiyaporn, 2008] and manganese to water. Therefore, in this work we are interested to develop methods for measurement some water quality parameters such as iron, manganese, phosphate and ammonium for assessment of water quality in Ping river. An analyzer for multi-parameter analysis based on sequential injection analysis (SIA) and simple colorimetric detection was developed for determination of these parameters in water samples.

Туре	Classification	Parameters		
1	Coloration/Appearance/Odor	Turbidity, SS, pH, TOC, Cu, Mn, Fe		
2	Chemical toxicity to human	NO3 ⁻ , Cd, As, Cu, Zn, Pd, Mn, Cr, Fe, Ca, Mg		
3	Biological toxicity to human	T.Coli, E.Coli		
4	Conservation of aquatic ecosystem	DO, BOD, COD, NH ₄ , NO ₃ ⁻ , Zn, Cu, Cd, Ni, Mn, Pd, As, PPCPs		
5	Eutrophication	TN, TP		

Table 1.1 Classification of water quality parameters





1.2 Sequential Injection Analysis (SIA)

Sequential injection analysis (SIA), which is one of flow-based analytical techniques, was developed by Ruzicka and Marshall in 1990 based on the same principle as flow injection analysis (FIA), but SIA has advantages over FIA in terms of automation, simplicity, ease, and flexibility. Various variables can be efficiently controlled by a computer, and has high flexibility to modify for determination of different analytes through software control of the system parameters rather than physical changes to the hardware [Cladera, 1995, Cerda, 2014, Zagatto, 2012]. The simple SIA system are shown in Figure 1.2, the components of the system are a syringe pump with only one of a liquid driver, a multi-port selection valve which is the important part of the SIA [Zagatto, 2012, Mesquita, 2009], a holding coil, and a detector. Normally, the multi-port selection valve comprises 6-10 peripheral ports and a central port is linked to a holding coil, and other peripheral ports are connected to different solution aspiration tubes, and different manifold components such as detector, mixing chamber, and column etc. The actuation of the solution and mixing of the solution in the mixing tube is controlled by bi-directional piston of syringe pump. The SIA system is altogether computer controlled and the injection volumes, residence times, delivery of solutions and analytical path lengths are based on a valve timing sequence and flow rates [Zagatto, 2012]. The computer selects port of the valve to be connected to its side port, start and stops the syringe pump in order to aspirate or dispense solutions, selects volume and adjusts the flow rate. In addition the computer is used for data recording and processing [Cerda, 2014].

The SIA operates under laminar flow of solution. As shown in Figure 1.3, dispersion in an SIA system leads to the sample and reagent zone overlapping, and the product (P) formation to be detected [Cerda, 2014]. A degree of mixing depends on moving the sample zone forward and backward in several steps (n) of sufficient length (L). Mixing efficacy promoted the combination of molecular diffusion and the flow defined on the liquid that pushes/pulls the fluids. In fact, the most of sequential injection systems, the sample homogenization is based on overlap of adjacent zones, which depends on the sampleand reagent volumes involved, manifold geometry and timing [Zagatto, 2012].



Figure 1.3 The flow characteristics sample and reagent in the SIA system, P: product, R: reagent, S: sample [Cerda, 2014]

1.3 SIA colorimetric analysis

Colorimetric analysis is a method for determining concentration of a chemical element or chemical compound in a solution with the aid of a coloring reagent. It is applicable to both organic compounds and inorganic compounds and may be used with or without an enzymatic stage [Colorimetric analysis, 2015]. In colorimetry, the transmission of light and its absorbance have very specific meanings with analyte. These are:

Transmittance (T) = $\frac{Light \ transmitted \ (l)}{Incident \ light \ (I_0)}$ Absorbance = log (1/T) = abc

Where: "a" is constant (the ability of a given molecule to absorb a particular wavelength of light)

"b" is the path length (the longer the path, the less light gets through)

"c" is the concentration (the more molecules in the solution, the more light is absorbed)

To get a straight line calibration curve, absorbances vs. concentrations have to be plotted. The equation of colorimetry used for the calibration curve is Beer's Law (is the Transmitted light = Initial light x $10^{(-abc)}$

A colorimeter consists of a light source, a filter, a sample cell, and a detector. In a simple colorimeter, the light source can be a Light Emitting Diode (LED). The advantage of using LED is longer battery life and its temperature stability which does not shift wavelength when temperature changed. The filter removes all light except the wavelengths used for the analysis. The detector determines how much light was transmitted through the sample for correlation to concentration of analyte. Most of the species in water do not have any color, therefore, the species do not absorb light in the visible region. To measure the absorbance of the colorless molecules, a reaction must produce a colored product that can be measured. Many approaches are available such as the formation of the chelate by complexation reaction between the analyte species and reagent, which has a different color from either the species or the reagent. The formation of an intermediate compound that can be oxidized or reduced afterwards to give a colored compound, or use of colored reagent which is bleached by the species being analyzed *etc.* Developing a test includes finding the optimum pH for reaction and color development, "masking" of possible interferences, and determining optimum time

for measurement [Orion Colorimetry Theory, 2015]. The main advantages of the colorimetric assay are its rapidity, precision, simplicity, low cost, accuracy and the lack of any radioisotope [Mosmann, 1983, Rahman, 2004].

1.4 Iron

1.4.1 General background

Iron is one of heavy metal, which presents in the soil and rock and can be refeased into water sources. Its common soluble forms includes bivalent iron (such as iron(II) ion (Fe²⁺) or iron(II) hydroxide ion (Fe(OH)⁺)), and trivalent iron (such as iron(III) (Fe³⁺) or ferric(III) hydroxide) or bacterial form [Chaturvedi, 2012]. Iron in water affects to cause problems about color and odor [Cho, 2005]. Although iron is a harmless element present in public and private water supplies, high concentration of dissolved iron can result in poor tasting, unattractive water that stains both plumbing fixtures and clothing. Ferric iron deposits within corroded pipes can break free and generate rusty tap water [Colter, 2006]. The average iron concentration in rivers has been reported to be 0.7 mg L⁻¹. In anaerobic groundwater where iron is in the form of iron(II), concentrations will usually be $0.5-10 \text{ mg } \text{L}^{-1}$, but concentrations up to 50 mg L^{-1} can sometimes be found. The drinking water standard has been defined for the amount of iron is 0.3 mg L⁻¹ [Environmental Services, 2003] but may be higher in countries where various iron salts are used as coagulating agents in water-treatment plants and where cast iron, steel, and galvanized iron pipes are used for water distribution [WHO, 2003]. by Chiang Mai University

Analytical techniques for determination of iron concentration have been developed and deployed, such as titrimetric, electrochemical, chromatographic, ultracentrifugation and photometric methods [Borman, 2009]. Colorimetric method is commonly used for the determination of trace amounts of iron involves the complexation of Fe^{2+} with 1,10-phenanthroline to produce an intensely red-orange colored complex.

1.4.2 Sequential injection analysis methods for iron determination

Sequential injection analysis was applied for determination of iron in various water samples. The relevant information such as analytical techniques and some characteristics of the system are summarized in Table 1.2.



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Technique	Sample	Linear range (mg Fe L ⁻¹)	LOD (mg Fe L ⁻¹)	RSD (%)	Throughput (h ⁻¹)	Ref.
Spectrophotometry	Artesian water	$0.04 - 4.0 (\text{Fe}^{2+})$ $0.10 - 5.0 (\text{Fe}^{3+})$	$0.04 (Fe^{2+})$ 0.09 (Fe^{3+})	<2.8 (Fe ²⁺)	_	[Kozak, 2015]
Spectrophotometry	Pharmaceuticals, waters and foods	$0.05 - 3.0 \ \mu g \ Fe^{3+}$ L^{-1}	0.03 μ g Fe ³⁺ L ⁻¹	<5.0	60	[Pragourpun, 2015]
Charged coupled device detector (CCD) spectrophotometer	Natural waters	0.10 - 2.0	0.01	<5.0	-	[Mesquita, 2013]
Spectrophotometry	Electroplating wastewater and environmental waters	1.0 - 40.0 μ g Fe ³⁺ L ⁻¹	$0.20 \ \mu g \ Fe^{3+} \ L^{-1}$	<2.2	14	[Gao, 2013]
Spectrophotometry	Water in the energy cogeneration system	0.13 - 12.5	0.04	<2.5	j -	[Mirabó, 2009]
Spectrophotometry	Industrial wastewater	0.1 - 5.0	0.03	1.8	18	[Ohno, 2006]

Table 1.2 Some researches on sequential injection analysis systems for determination of iron

Technique	Sample	Linear range (mg Fe L ⁻¹)	LOD (mg Fe L ⁻¹)	RSD (%)	Throughput (h ⁻¹)	Ref.
Diode array spectrophotometer	Tap water, soil, urine	1.0 - 10		3	27	[Staden, 2004]
Spectrophotometry	Natural and waste waters	0.05 - 6.0	0.05 (Fe ²⁺) 0.10 (Fe ³⁺)		20	[Galhardo, 2001]
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 Table 1.2 (Continued)

1.5 Manganese

1.5.1 General background

Manganese is a metallic element that contains in many types of rock and soil [Iron & manganese in groundwater, 2007]. Manganese present in water by percolation through soil and rock dissolves manganese enter water supplies. These constituents may be found in their reduced, soluble forms (Mn²⁺), or as oxidized, colloidal, particulate forms such as MnO₂ [Environmental Services, 2003]. Manganese is often found in waters that present iron [Dvorak, 2014]. Surface water does not contain high concentration of manganese because it reacts with oxygen in water to produce its oxide that settle out as sediment. Manganese forms a black residue and high concentrations of these sediments cause reddish-brown or black stains on laundry and household utensils [Lemley, 2005, McFarland, 1914]. In drinking water, manganese is regulated by secondary drinking water standards established by the U.S. Environmental Protection Agency for public water supplies because manganese in high levels can impart a bittersweet or metallic taste to drinking water, and cause offensive taste, odor, color, corrosion, foaming, or staining problems [Lemley, 2005]. For these reasons, the drinking water standard has been defined for the amount of manganese is 0.05 mg L^{-1} [Lemley, 2005, Environmental Services, 2003]. A typical value of dissolved manganese in surface water is less than 1.0 mg L^{-1} [The National Environmental Board, 1994]. Therefore, knowing the amount of manganese in the water is necessary.

1.5.2 Sequential injection analysis method for manganese determination

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The manganese determination in various sample using sequential injection analysis technique have been reported. Table 1.3 shown some researches on application of sequential injection analysis system to determine manganese.

Technique	Sample	Linear range (mg Mn L ⁻¹)	LOD (mg Mn L ⁻¹)	RSD (%)	Throughput (h ⁻¹)	Ref.
Flame atomic absorption spectrometry	Food	50 - 3000 μg L ⁻¹	0.50 µg L ⁻¹	<6.3	48	[Lemos, 2008]
Spectrophotometry	Soil	0.5 - 30	0.20	<5.6	-	[Somnam, 2008]
Spectrophotometry	River water and effluent streams	0.020 - 0.50 (Mn ²⁺) 0.025 - 0.55 (Mn)	0.01 (Mn ²⁺) 0.01 (Mn)	0.27 (Mn ²⁺) 0.34 (Mn ⁷⁺)	30	[Staden, 2003]
Spectrophotometry	Tap waters and effluent streams	1.0 - 7.0	0.62	≤3.0	50	[Naidoo, 2000]
		MAI U	NIVERSI			

Table 1.3 Some researches on sequential injection analysis systems for determination of manganese	

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1.6 Phosphate

1.6.1 General background

Phosphorus is generally considered to be the primary nutrient limiting aquatic plant growth, and is the key nutrient implicated in the eutrophication of fresh waters [Glennie, 2002]. Orthophosphate is the only form of P that autotrophs can assimilate. Extracellular enzymes hydrolyze organic forms of P to phosphate [Correll, 1998]. Phosphorus compounds, in particular orthophosphate PO_4^{3-} , are considered to be the limiting nutrients in most stagnant and flowing waters [WTW, 2003]. Phosphorus enters surface water bodies via non-point sources such as agricultural runoff and animal husbandry, and from point source municipal and industrial wastewater discharges [Glennie, 2002]. Phosphates stimulate the growth of plankton and water plants that provide food for fish. This may increase the fish population and improve the waterway's quality of life. If too much phosphate is present, algae and water weeds grow wildly, choke the waterway, and use up large amounts of oxygen. Many fishes and aquatic organisms may die [Important water quality factors, 2007]. As a result, a phenomenon called "Eutrophication" of the water with known effects such as increased growth of algae, oxygen depletion as far as anoxia in the deeper regions, etc. [WTW, 2003].

Measuring phosphate in aquatic environments can be a very important tool in understanding the health of a system or it's "water quality". Monitoring of phosphate levels in water can help identify possible sources for phosphate introduction to aquatic systems. Precautions can be taken to minimize these inputs and can prevent any harmful effects that can occur as a result of eutrophication. Phosphate determination is based on molybdenum blue reaction. The orthophosphate reacts with ammonium molybdate and potassium antimonyl tartrate in acidic solution to form a molybdophosphoric acid, which was then reduced by ascorbic acid to form molybdenum blue which has extinction at 885 nanometer wavelength. The intensity of the blue solution is related to the concentration of phosphorus in the water samples [Trilogy, 2015].

1.6.2 Sequential injection analysis method for phosphate determination

Some researches on sequential injection analysis method were reported for phosphate determination in water and other samples based on spectrophotometric technique. The analytical characteristics of the system can be summarized in Table 1.4.



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Technique	Sample	Linear range (mg PO4 ³⁻ L ⁻¹)	LOD (mg PO4 ³⁻ L ⁻¹)	RSD (%)	Throughput (h ⁻¹)	Ref.
Paired emitter- detector diode (PEDD)	Cola drinks	50 - 200	20	<2.0	21	[Saetear, 2013]
Fiber-optic charge coupled spectrometry	Natural water	0.2 – 10 μmol L ⁻¹	0.10 μmol L ⁻¹	0.8 - 3.0	20	[Khlyntseva, 2011]
Spectrophotometry	Water in the energy cogeneration system	<u>}</u> - 1	0.05	<2.5	-	[Mirabó, 2009]
Fluorescence spectrometry	Coastal waters	$\begin{array}{l} 0.5-1.0 \; \mu mol \; L^{-1} \\ 1.0-5.0 \; \mu mol \; L^{-1} \end{array}$	0.05 μmol L ⁻¹	<u>]]-</u>	270	[Frank, 2006]
Diode array spectrometry	beverages, wastewaters and urine	0.3 - 20	100 μg L-1	<2.4	18	[Mas-Torres, 2004]
Double-beam spectrophotometer	Urine	$0.05 \times 10^{-2} - 3 \times 10^{-2}$	iang <u>M</u> ai U rese	3.9 8	30 75	[Themelis, 2004] [Galhardo, 2000]
specifophotometry	Liiviioinnental	0.2 - 7.0	0.10	-	15	[Camaru0, 2000]

Table 1.4 Some researches on sequential injection analysis systems for determination of phosphate

1.7 Ammonium

1.7.1 General background

Ammonia is the preferred nitrogen-containing nutrient for plant growth. Its chemical formula is NH_3 in the un-ionized state and NH_4^+ in the ionized form. Total ammonia is the sum of both NH₃ and NH₄⁺. Total ammonia is what is measured analytically in water [Ammonia, 2015]. A chemical reaction also occurs when ammonia dissolves in water. In aqueous solution, ammonia acts as a base, acquiring hydrogen ions from H₂O to yield ammonium and hydroxide ions [Shakhashir, 2008]. Natural levels in groundwater are usually below 0.2 mg L⁻¹. Higher natural contents (up to 3 mg L⁻¹) are found in strata rich in humic substances or iron or in forests. Surface waters may contain up to 12 mg L⁻¹. Ammonia may be present in drinking-water as a result of disinfection with chloramines [WHO, 1996]. Natural factors that can affect the concentration of ammonia in water including of algal growth, decay of plant or animal material, and fecal matter. Other aspects of nitrogen cycling can also affect the amount of ammonia present. Ammonia can also come from domestic, industrial or agricultural pollution, primarily from fertilizers, organic matter or fecal matter [Ammonia, 2015]. The presence of ammonia at higher than geogenic levels is an important indicator of pollution. Taste and odour problems as well as decreased disinfection efficiency are to be expected if drinking-water containing more than 0.2 mg L⁻¹ of ammonia is chlorinated, as up to 68% of the chlorine may react with the ammonia and become unavailable for disinfection [WHO, 1996]. Therefore, the measurement of trace amounts of ammonium in water is necessary. One of method for determination of ammonium in water is by the reaction of ammonia with a phenol and hypochlorite reagent to give indophenol which has extinction at 650 nanometer wavelength.

1.7.2 Sequential injection analysis method for ammonium determination

Spectrophotometric methods for determination of ammonium have been reported. Sequential injection analysis system was applied for ammonium measurement in water and environmental samples as summarized in Table 1.5.

Sample	Linear range (mg NH4 ⁺ L ⁻¹)	LOD (mg NH4 ⁺ L ⁻¹)	RSD (%)	Throughput (h ⁻¹)	Ref.
	1000	000 4	Sol		
Water	5.0 -150 µmol L ⁻¹	1.80 μmol L ⁻¹	0.6	17	[Infante, 2011]
110	3///	ON'	131		
Water in the energy		*			
cogeneration	3.3 - 20	1.0	<2.5	-	[Mirabó, 2009]
system		(KY			
River and marine		10 11-1	12	100	
waters	$0.0 - 20 \ \mu mol L^{-1}$	$1.0 \ \mu mol L^{-1}$	21	120	[Frank, 2006]
Water and	120	THE Y	÷//		
industrial effluent	0.0 - 50	0.36	1.8	16	[Staden, 1997]
streams	al l	JNIVE			
F		0.50	2.5		100 (1
Environmental	0.0 - 60	0.60	3.5 1800 MU		[Oms, 1996]
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	Sample Water Water in the energy cogeneration system River and marine waters Water and industrial effluent streams Environmental	SampleLinear range (mg NH4+ L ⁻¹)Water $5.0 - 150 \ \mu mol \ L^{-1}$ Water in the energy cogeneration $3.3 - 20$ systemRiver and marine waters $0.0 - 20 \ \mu mol \ L^{-1}$ Water and industrial effluent $0.0 - 50$ streamsEnvironmental $0.0 - 60$	SampleLinear range (mg NH4+ L^-1)LOD (mg NH4+ L^-1)Water $5.0 - 150 \ \mu mol \ L^{-1}$ $1.80 \ \mu mol \ L^{-1}$ Water in the energy cogeneration $3.3 - 20$ 1.0 System $3.3 - 20$ 1.0 River and marine waters $0.0 - 20 \ \mu mol \ L^{-1}$ $1.0 \ \mu mol \ L^{-1}$ Water and industrial effluent $0.0 - 50$ 0.36 Streams $0.0 - 60$ 0.60	Sample Linear range (mg NH4 ⁺ L ⁻¹) LOD (mg NH4 ⁺ L ⁻¹) RSD (%) Water $5.0 - 150 \ \mu mol \ L^{-1}$ $1.80 \ \mu mol \ L^{-1}$ 0.6 Water in the energy cogeneration $3.3 - 20$ 1.0 <2.5 system $0.0 - 20 \ \mu mol \ L^{-1}$ $1.0 \ \mu mol \ L^{-1}$ $-$ River and marine waters $0.0 - 20 \ \mu mol \ L^{-1}$ $1.0 \ \mu mol \ L^{-1}$ $-$ Water and industrial effluent $0.0 - 50$ 0.36 1.8 Environmental $0.0 - 60$ 0.60 3.5	Sample Linear range (mg NH4 ⁺ L ⁻¹) LOD (mg NH4 ⁺ L ⁻¹) RSD (%) Throughput (h ⁻¹) Water $5.0 - 150 \mu mol L^{-1}$ $1.80 \mu mol L^{-1}$ 0.6 17 Water in the energy cogeneration system $3.3 - 20$ 1.0 <2.5 $-$ River and marine waters $0.0 - 20 \mu mol L^{-1}$ $1.0 \mu mol L^{-1}$ $ 120$ Water and industrial effluent streams $0.0 - 50$ 0.36 1.8 16

 Table 1.5 Some researches on sequential injection analysis systems for determination of ammonium

1.8 Aim of these studies

The main objectives of this research project are:

1.8.1 To develop SIA system for multi-parameters analysis such as ammonia, phosphate, manganese and iron for water quality measurement.

1.8.2 To apply the developed system for analysis of water samples from Ping river of Chiang Mai province.



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