

CHAPTER 1

INTRODUCTION

1.1 Introduction

Pickle is one of the favorable food preservation method, which is used in household and industry. Salt is the necessary material used in pickling cause of an antiseptic and preservative properties (Kaufmann, 1971). Thus, wastewater from pickling factory contains high concentration of sodium chloride and a lot of organic matter. The high salinity is the main problem of wastewater discharged from pickling factory to surrounding area, especially affected to surface water and contaminated to ground water.

Pickling wastewater is listed as hazardous waste in most industrial countries, mainly due to their corrosive properties. In Thailand, the wastewater from pickling food factories has still not yet been inappropriate consideration in terms of monitoring the chloride concentration and treatment before discharging. Thus, many pickling factories try to reduce the chloride concentration in wastewater by dilution method before release the water to natural river, which may cause more environmental problems. Moreover, in case of high chloride concentration, dilution is not possible. Some factories build the concrete pit to store the wastewater and let it evaporating by sunlight causing very bad smell (Sastraruji, 2003).

Therefore, the monitoring task of chloride content in water, especially in the affected area around a pickling factory, is necessary to have a general assessment of water quality in terms of salinity.

1.2 Characteristics of wastewaters from pickling food factory

There has been relatively less information in available the literature on the polluted characteristics of wastewaters from pickling manufacture. Results of previous studies are summarized in Table 1.1 and Table 1.2, the spent brine characteristics are compared with ordinary domestic sewage, which seems weak in comparison (Brown *et al.*, 1973). In general, pickling wastewaters are characterized by high dissolved solids, low pH due to the fermentation process, high chloride content and high BOD.

Table 1.1 Characteristics of wastewater from pickling manufacture (Linda *et al.*, 1976)

Reference	pH	BOD	Cl ⁻	TS	SS
		mg.l ⁻¹			
Ryan (1940)	4.0	3,000	-	4,000	200
Haseltine (1952)	4.0	2,000	6,500	13,600	200
Barnes and Weinberger (1958)	3.6 – 4.4	800 – 5,400	2,500 – 14,000	-	-
Kimball (1960)	4.0 – 6.0	-	-	-	-
Nemerow (1963)	3.9 – 8.8	1,070	3,000	8,000 – 24,000	148

Table 1.2 Brine wastewater in comparison with typical domestic sewage (Brown *et al.*, 1973)

Parameters	Brine	Sewage
TOC, mg/l	3,400	124
SS, mg/l	330	170
Kjeld-N, mg/l	732	31

TP, mg/l	87	10
Cl ⁻ , g/l	111	< 1
pH	3.4	7.2

1.3 Salinity

Salinity is an important measurement in the analysis of certain industrial wastes and seawater. It is defined as the total solids in water after all carbonates have been converted to oxides, all bromide and iodide have been replaced by chloride, and all organic matter has been oxidized.

Associated terms are chlorinity, which includes chloride, bromide, and iodide, all reported as chloride, and chlorosity, which is the chlorinity multiplied by the water density at 20°C. An empirical relationship between salinity and chlorinity often is used:

$$\text{Salinity, } \text{‰} = 0.03 + 1.805 (\text{chlorinity, } \text{‰})$$

(APHA, AWWA, WPCF, 1985).

In this case to assess the salinity in water around a pickling food factory, the chloride parameter was selected to analyze because Cl⁻ is dominated species in this kind of factory's discharged water.

Table 1.3 below shown the salinity classification suitable for irrigation waters.

Table 1.3 Salinity classes for irrigation waters (National Academy Press, 1990)

Irrigation water	Salts, mg.l ⁻¹	Crop problem
1. Fresh	< 125	None
2. Slightly saline	125 – 250	Rare

3. Moderately saline	250 – 500	Occasional
4. Saline	500 – 2,500	Common
5. Highly saline	2,500 – 5,000	Severe

1.4 Chloride and its effects

All natural waters contain dissolved salts in one concentration or another. The only exception is rain water, which may acquire a small salt load from impurities in the air. In addition to natural waters, industry also produces saline waters which are not suitable for direct further use. In practice, many types of saline water, which also includes the respective salt content, are frequently encountered. It is only seldom possible to use these waters directly. For most applications, it is necessary to reduce the salt content to the target level, especially for industrial water as 0.02 to 0.75 g/l. A further point to be considered is that effluent introduced into the receiving water must meet national or supranational anti-pollution standards (Heitmann, 1990).

Chloride is usually present in natural waters. A high concentration occurs in waters that have been in contact with chloride-containing geological formations. Otherwise, a high chloride content may indicate pollution by sewage or industrial wastes or by the intrusion of seawater or saline water into a freshwater body or aquifer. A salty taste in water depends on the ions with which the chlorides are associated. With sodium ions the taste is detectable at about 250 mg.l⁻¹.

The chloride concentration is higher in wastewater than in raw water because sodium chloride is a common article of diet and passes unchanged through the digestive system (APHA, 1985). At high salinity in water, it caused some adverse effects to human and plant growth. There are some studies had been

proved this above effects. A high chloride content has a corrosive effect on metal pipes and structures and is harmful to most trees and plants (Bartram and Ballance, 1996). Water potential and osmotic potential of plants became more negative with an increase in salinity (Khan *et al.*, 1999). For irrigation activities, the high salinity in root zone of irrigated plants has been making it difficult for crops to take up water due to osmotic pressure differences between the water outside the plants and within the plant cells (Sawyer *et al.*, 1994). In observation of plant behaviour, the most common visual symptom is slower and more stunted growth or no growth at all on very saline areas. A darker green colour as well as greater leaf succulence may be evident. However, in most cases, yield will be the only evident response to indicate salinity, in fact dry matter production may be less affected than yield. Osmotically stressed plants show no distinctive symptoms apart from the above and those related to normal water stress (Shaw *et al.*, 1987).

Chloride in reasonable concentrations is not harmful to humans. At concentrations above 250 mg/l they give a salty taste to water, which is objectionable to many people. For this reason chlorides are generally limited to 250 mg/l in supplies intended for public use (Sawyer *et al.*, 1994).

1.5 Methods for chloride determination

1.5.1 Standard methods

The current standard methods for chloride analysis recommended by APHA including:

- Argentometric method (Mohr method): is suitable for use in relatively clear waters when 0.15 to 10 mg chloride are present in the portion titrated. This method uses potassium chromate as indicator to indicate the end point of the silver nitrate titration of chloride. Silver chloride is precipitated quantitatively before red silver chromate is formed.

- Mercuric nitrate method: is suitable for the chloride concentration in portion less than 10 mg. Chloride can be titrated with mercuric nitrate, because of the formation of soluble, slightly dissociated mercuric chloride. The diphenylcarbazone indicates the titration end point by formation of a purple complex with the excess mercuric ions.
- Potentiometric method: is suitable for colored or turbid samples in which color indicated end points might be difficult to observe. Chloride is determined by potentiometric titration with silver nitrate solution with a glass and silver-silver chloride electrode system. The end point of the titration is that instrument reading at which the greatest change in voltage has occurred for a small and constant increment of silver nitrate added.
- The ferricyanide method: is an automated technique. Thiocyanate ion is liberated from mercuric thiocyanate by the formation of soluble mercuric chloride. In the presence of ferric ion, free thiocyanate ion forms a highly colored ferric thiocyanate, of which the intensity is proportional to the chloride concentration.

(APHA, AWWA, WPCF, 1985).

Besides the above methods, with the development of automated tools and the “greener analytical chemistry” trend (Rocha *et al.*, 2001), the flow injection analysis (FIA) method developed in the mid 1970 (Harvey, 2000) and now the sequential injection analysis (SIA) in 1990 (Ruzicka *et al.*, 1990) are the new heading of analytical chemistry with multi-advantages such as using less sample and reagent volumes, reducing time consumption, a automated procedure entirely controlled by computer etc.

In this research, the sequential injection analysis (SIA) with the potentiometric detection which has been developed by other members of the research group was employed to determine the chloride content in surface water around a pickling food factory. Besides, the standard Argentometric method (Mohr method) was also used as a reference method for comparison.

1.5.2 The methods employed in this work

1.5.2.1 Sequential Injection Analysis (SIA)

Sequential injection analysis is an advanced technique was reported by Ruzicka and Marshall in 1990 for automatic sample analysis, based on a similar principle of flow injection analysis (FIA). The SIA offers many advantages over the original one such as: the instrumental simplicity, ease and efficiency with which hydrodynamic variables can be controlled. Thus, this new technique has been widely accepted as new selection for both research and industrial analysis laboratories (Cladera *et al.*, 1995).

Principle

Whereas FI uses a multi-channel pump and uni-directional (forward) flow, SI uses a single-channel pump to move the column of liquid in reverse and forward steps through a channel, and which consists of a holding coil, multi-position valve and detector (Figure 1.1). The multi-position valve serves as a central distributor through which appropriate volumes of liquid segments are sequenced by aspiration into the holding coil (HC) and then propelled by a flow reversal into the detector. Both FI and SI systems operate on identical underlying principles: sample injection, controlled dispersion and reproducible timing. Therefore, the design of the sequential injection systems also follows the established rules for providing limited, medium or high dispersion of the injected sample zones. The dispersion coefficients of sample and reagent(s) have to be carefully considered when developing an assay. This allows the proportion of reagent to be selected by choosing a delay time t_d that produces optimum conditions for reaction rate measurement (Figure 1.2) performed during the stopped flow. When the sample zone moves through the detector without stopping, a peak similar to that obtained by first-generation FI is recorded (heavy shaded area in Figure 1.2). Note, however, that such a peak is narrower than the

sum of the two injected zones, as the sample and reagent zones can never overlap completely (Ivaska *et al.*, 1993).

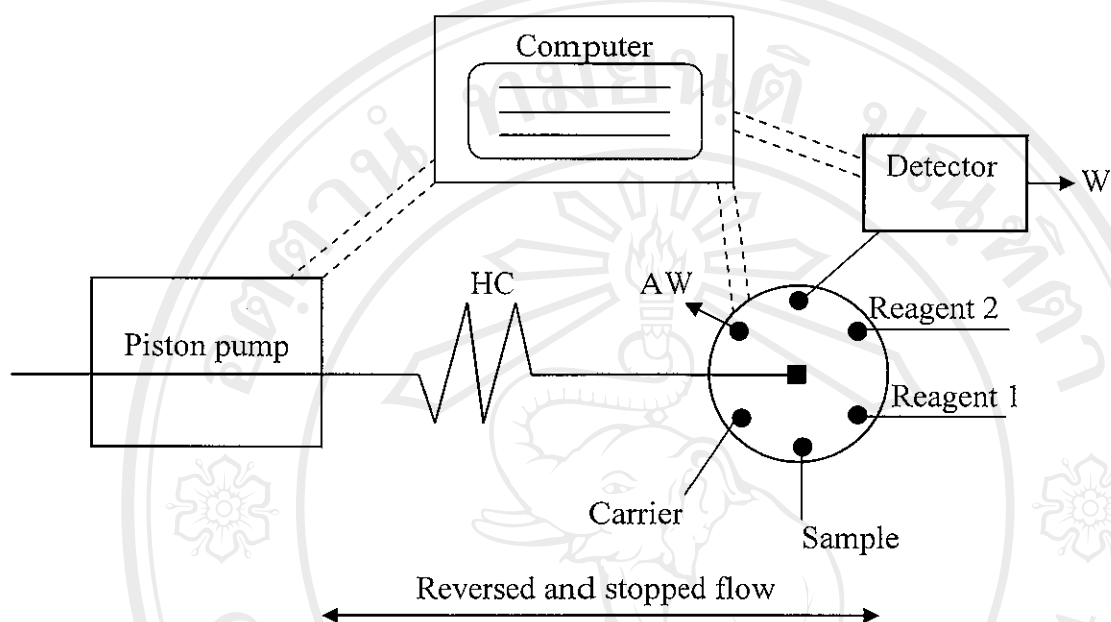


Figure 1.1 Typical sequential injection system utilizing programmed forward, reversed and stopped flow. HC, Holding coil; AW, auxiliary waste; and W, waste (Ivaska *et al.*, 1993)

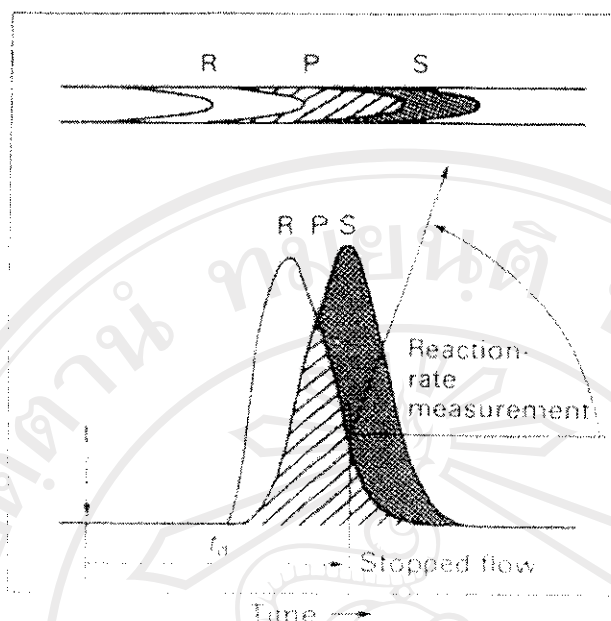


Figure 1.2 Sequenced zones of reagent (R) and sample (S) intersperse during flow reversal while the detectable product (P) is formed. On arrival at the detector a suitable section of the product zone is captured within the observation field of the detector by selecting a stop delay time t_d for reaction-rate measurement (Ivaska *et al.*, 1993)

System configuration

A sequential injection system has been designed and is depicted in Figure 1.3 (top) together with a typical chart recorder plot (below). Each measurement starts by aspirating a wash solution, followed by sample injection (S), reagent injection (R) and measurement during a backward movement of the piston of a syringe-type pump. In this way well defined zones are injected sequentially into a conduit which serves as a reactor (R), flow-through detector (D) and holding reservoir (H). Mutual dispersion of the injected zones is achieved through the preprogrammed movement of these zones towards the detector. The measurement cycle is terminated when the flow is reversed and the mutually dispersed zones are propelled back through the system and finally to waste (Ruzicka *et al.*, 1990).

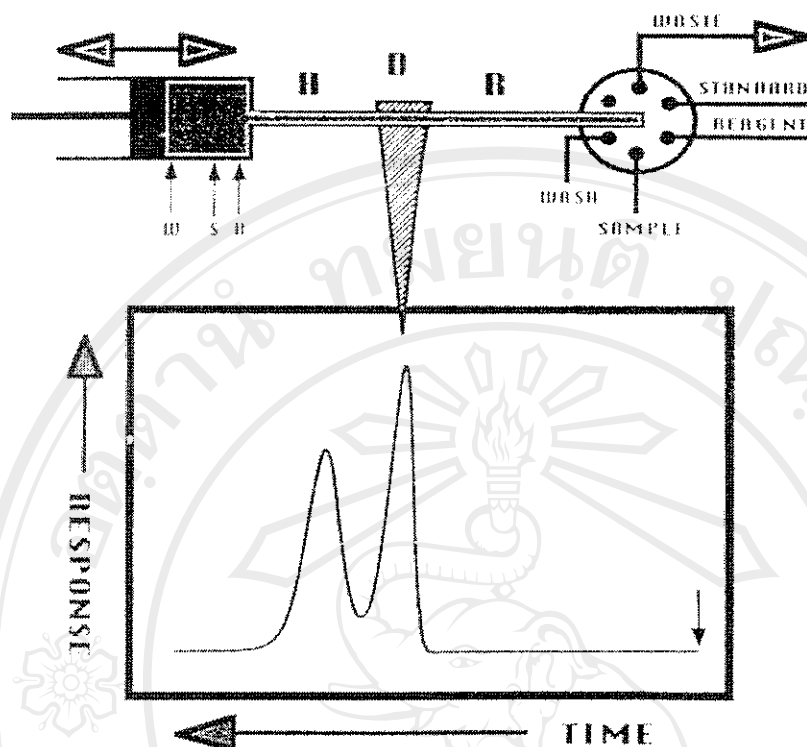


Figure 1.3 Principle of sequential injection technique showing manifold (top) and readout (below). The plunger of the piston pump moves in discrete steps to aspirate wash solution (W), sample solution (S) and reagent solution (R) into a channel which consists of reaction (R), detection (D) and hold-up (H) sections. The selector valve provides sequential injection of the solutions into the channel through preprogrammed steps synchronized with piston movement. The record (below) shows a typical double peak, the trough of which is located at the time when the flow has been reversed (Ruzicka *et al.*, 1990)

Advantages of SIA

As with FIA, high sample throughputs are achievable (about 200 analyses h^{-1}) thus providing the potential of pseudo-continuous process monitoring. The major advantage of SIA is its ability to perform numerous complex chemistries

coupled with various modes of detection without reconfiguration of the flow manifold. In addition SIA requires very low sample and reagent volumes ($\mu\text{l analysis}^{-1}$), thus leading to minimal effluent.

Other than the multi-position port the remaining components of an SIA instrument are the same as in automated FIA. Propulsion of solution through the manifold tubing (typically 0.5-0.8 mm I.D. PTFE) is usually achieved using a syringe pump, although other pumps including peristaltic and sinusoidal flow types have found some applications.

One component that is essential to the operation of an SIA is a computer fitted with an interface card and software for control of the timing and operation of the pump and valve as well as data acquisition.

It can be seen therefore, that with the addition of a multi-position port and relevant software, the conversion of an automated FIA to an SIA instrument is a relatively simple procedure (Barnett *et al.*, 1999).

The SIA method used in this work has been developed by other members of the research group.

1.5.2.2 Potentiometric detection

Potentiometric detection is based on the measurement of the electromotive force of the measuring cell, which usually consists of a suitable indicating electrode (whose potential depends on the concentration or, the activity of the analyte) and of a reference electrode, maintained at a constant potential during the measurement. The measurement of the potential difference between these electrodes is carried out with a potentiometer of high input impedance, which prevent electrode processes that might disturb the equilibrium at the electrode-solution interface. Ion selective electrodes with various membranes are the most common indicating electrodes in modern potentiometry (Trojanowicz, 2000).

To analyze chloride in water, the simple Ag/AgCl electrode is usually used. The response of electrode involves the reduction of silver ion, $\text{Ag}^+ + \text{e}^- = \text{Ag}$

and the oxidation of chloride ion, $2\text{Cl}^- - 2e = \text{Cl}_2$. Depending on complexity of the material which is used as the sensing membrane, the response of the electrode may involve any of the following sequence of steps:

- a. Reduction (activity differences)
- b. Solubility equilibria
- c. Complexing solubility equilibria (or ion-exchange)

When membrane comes in contact with a solution containing chloride ions, a potential develops across the membrane. This potential is measured against a constant reference potential with a standard pH/mV meter or an ion meter and depends on the level of free chloride ions in the solution which can be described by the Nernst equation:

$$E = E_o + S \log X$$

where:

E: measured electrode potential

E_o : reference potential (a constant)

S: electrode slope (theoretically $S = 2.303RT/nF$)

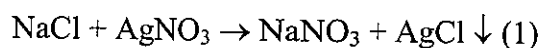
X: level of chloride in solution. X represents the effective concentration of free chloride ions in the solution.

The most important interfering ions of chloride determination by ion selective electrode are Hg^{2+} , Br^- , I^- , S^{2-} , CN^- , $\text{S}_2\text{O}_3^{2-}$ (Fricke *et al.*, 1977).

1.5.2.3 Argentometric method (Mohr method)

Principle

In a neutral or slightly alkaline solution, potassium chromate (K_2CrO_4) can indicate the end point of the silver nitrate titration of chloride. The reactions are occurred as follows:



The water sample is mixed with an indicator, potassium chromate, to produce the prepared solution. The liquid will be transparent yellow due to the chromate ion. This mixture contains both the chloride ions and the chromate ions in solution. The prepared solution is then titrated with silver nitrate until the solution changes from yellow to pink-orange. The reaction takes place in two steps. The silver nitrate reacts with the chloride ions from the water sample to produce insoluble white silver chloride. When all the chloride ion has been converted to silver chloride, the remaining silver nitrate will react with the chromate, the indicator, to form the pink-orange colored silver chromate precipitate. This color change signals the end of the reaction given above. The amount of silver nitrate used is convertible to the amount of chloride in the original water sample. This standard method has been used in comparison the data with the sequential injection potentiometric method (Harvey, 2000).

1.6 Other supporting parameters

In order to have a general assessment of water quality around a pickling food factory in terms of salinity, some other parameters were used for supporting the data. Here are these selected parameters: pH, temperature ($^{\circ}\text{C}$), conductivity ($\mu\text{S}/\text{cm}$), total dissolved solids TDS (mg/l), dissolved oxygen DO (mg/l).

1.6.1 pH

pH is a term used rather universally to express the intensity of the acid or alkaline condition of a solution. It is a way of expressing the hydrogen-ion concentration, or the hydrogen-ion activity.

The pH scale is usually represented as ranging from 0 – 14, with pH 7 at 25°C representing absolute neutrality, acid range is from 0 – 7 and alkaline range is from 7 – 14 (Sawyer *et al.*, 1994).

Due to the characteristic of the pickling manufacture (fermentation process), the wastewater from this processing may be turned to acidic property. Therefore, the pH parameter was used to evaluate this property.

1.6.2 Dissolved oxygen (DO)

Natural waters in equilibrium with the atmosphere will contain dissolved oxygen concentrations ranging about 14.5 to 5 mg O₂ per liter depending on the water temperature, salinity, and altitude. The solubility of oxygen decreases as temperature and salinity increase. Determination of DO concentration is a fundamental part of a water quality assessment since oxygen is involved in, or influences, nearly all chemical and biological processes within water bodies (Chapman, 1996). In situ measurements of this parameter can be used as a primary indicator of water quality. DO could be measured by electrometric method and Winkler titration method (Burden *et al.*, 2002). The following table shows the relationship of dissolved oxygen (mg/l) to temperature and salinity.

Table 1.4 The relationship of DO, salinity and temperature

Oxygen Saturation (ppm) based on Temperature and Salinity						
Temp. (°C)	Salinity (ppt)					
	0	9	18.1	27.1	36.1	45.2
0	14.62	13.73	12.89	12.10	11.36	10.66
10	11.29	10.66	10.06	9.49	8.96	8.45
20	9.09	8.62	8.17	7.75	7.35	6.96
25	8.26	7.85	7.46	7.08	6.72	6.39
30	7.56	7.19	6.85	6.51	6.20	5.90

40	6.41	6.12	5.84	5.58	5.32	5.08
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Source: http://www.sensorex.com/support/education/DO_education.html

1.6.3 Temperature

Temperature of water is important to many of the chemical, physical, and biological processes. One of the important effects of temperature is on the rate of chemical and biological reactions, for example the solubility of oxygen in water increases as temperature decreases (Burden *et al.*, 2002). At different temperature the solubility of substances are also changed. The table below is shown the solubility in temperature function.

Table 1.5 Solubility of solutes as a function of temperature (mg of solutes per liter of water)

Solute mg/l	Temperature (°C)					
	0	20	40	60	80	100
O ₂	69	43	31	14	0	
CO ₂	3350	1690	970	580		
NaCl	357,000	360,000	366,000	373,000	384,000	398,000
KCl	276,000	340,000	400,000	455,000	511,000	567,000

Source: http://www.sensorex.com/support/education/DO_education.html

1.6.4 Conductivity

Conductivity is a measure of the electric current-carrying ability of water and is related to the concentration of dissolved ions present. In situ measurement of electrical conductivity in freshwaters provides an instantaneous estimate of the dissolved solids concentration, whereas in marine waters it is used commonly to measure the salinity (Burden *et al.*, 2002). The conductivity data got could be shown the relative salinity content in the water samples, so this data can support the salinity data in terms of site-comparison salinity content.

1.6.5 Total Dissolved Solids (TDS)

Total Dissolved Solids (TDS) are comprised mainly of ions such as iron, chloride, sodium, sulfate, etc. TDS is also related closely to conductivity data (K). Depending on whether waters are dominated by chloride or sulfate, the relationship typically might range from $\text{TDS (mg/l)} = 0.64K$ ($\mu\text{S/cm}$, chloride-dominated waters) to $\text{TDS (mg/l)} = 0.765K$ ($\mu\text{S/cm}$, sulfate-dominated waters) (Evangelou *et al.*, 1988).

1.7 Design of a monitoring program

This research is followed the trend of monitoring work. Therefore, a design of monitoring program is necessary. Below is a figure of steps in designing monitoring program that this research was followed (Harrison, 1992).

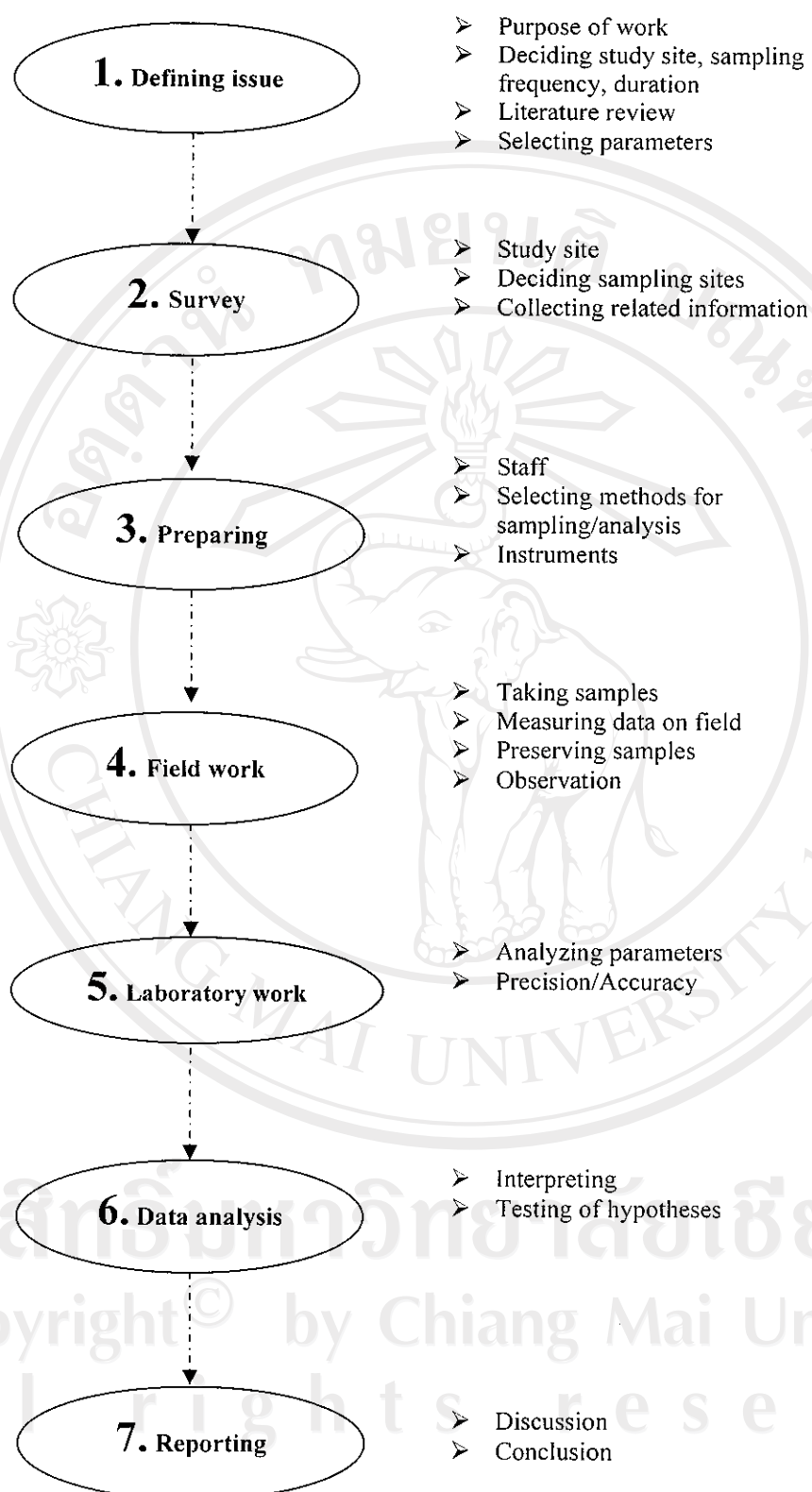


Figure 1.4 Steps in the design of a monitoring program

1.8 Research objectives

The following objectives were aimed:

- To determine the concentration of chloride in surface water around a pickling food factory;
- To verify a new procedure for chloride analysis; and
- To assess the surface water quality around the factory in terms of salinity.