# 1. INTRODUCTION

## 1.1 Background Information

Paraquat (1,1'-dimethyl,4,4'-bipyridyl) is a non-selective contact herbicide which is used world-wide[1,2]. It is the only pesticide which is locally produced in Thailand and its production in 1988 was about 7500 tons. The consumption rate of this compound is increased steadily[3,4]. There are at least 50 commercial trade names of paraquat available in Thailand[5]. Paraquat is used in either highland or lowland agriculture as preplanting, pre-harvest desiccant and non-crop land weed control substance[6-8].

It has been known that when paraquat is used in normal application either as aquatic herbicide or inland herbicide, no adverse environmental effect has been observed mainly because of its rapid and strong adsorption to clay minerals and degradation by photochemical process[1,8-10]. For human toxicity, up to present, the epidemiological data shows that paraquat is still in the first list of pesticides which cause deaths in the reported cases of pesticide poisoning in Thailand[4,11]. Most of the paraquat poisoning cases caused by suicide and accidental swallowing of liquid concentrate paraquat from unlabelled bottles or containers which had been stored inappropriately[1,4]. In 1992 Apisariyakul et al[7] and Vichairat[12] reported that there were severe cases of unintentional paraquat poisoning in Chiang Mai and Lamphun Province. Such cases have resulted in several versions of interpretation but no conclusive data have been established yet.

Since paraquat is cationic, very soluble in water and practically insoluble in organic solvents[13,14], liquid-liquid extraction is hardly used as its sample preparation. Cation exchange resin is therefore used to cleanup and concentrate paraquat, but this sample preparation still has some disadvantages [15,16]. Up to present, solid phase extraction (SPE) has become more widely used for sample preparation[17,18].

## 1.2 Paraquat

### 1.2.1 Physical and Chemical Properties

Paraquat was originally synthesized by the Imperial Chemical Industries Ltd. by coupling pyridine in the presence of sodium in anhydrous ammonia and quaternizing 4,4′-bipyridyl with methyl chloride as shown in Figure 1.1[1,19].

Pure paraquat salts are white and the technical products are yellow that decompose at $300^0$c. They are crystalline, odorless, hygroscopic powders with the molecular weight 257.2 for paraquat dichloride or 186.2 for paraquat ion. Paraquat is very soluble in water with its solubility around 700 g/l, but it is slightly soluble in alcohol and practically insoluble in organic solvents. It is non-explosive and non-flammable in aqueous formulation but corrosive to metals[1,13,14]. Its vapour pressure is less than 0.01 mPa at $20^0$c[5]. It is stable in acid or neutral

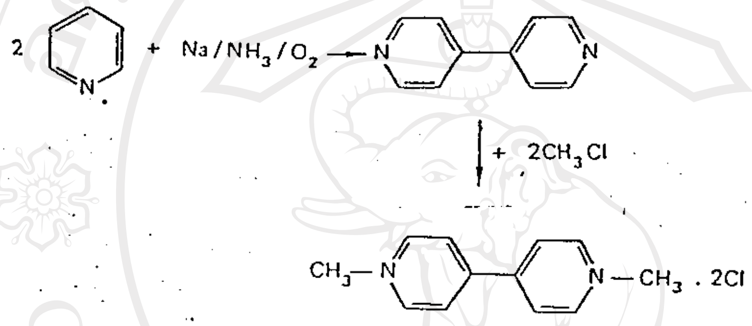

Figure 1.1 Synthesis of paraquat[1].

solutions but is readily hydrolysed by alkaline. Paraquat also readily undergoes a single-electron reduction to the cation radical with the standard redox potential, $E^0$, -0.54v [1,2,20].

### 1.2.2 Use and Mechanism of the Herbicidal Effect

Paraquat is a total non-selective contact herbicide. It is used to control weeds on crop land and non-crop land. It can be used as a desiccant and defoliant[1,2,5,14]. Paraquat is also very suitable for controlling aquatic weeds. Application rate usually ranges from 250-1500 g/ha, but, for grass and stubble, up to 2200 g/ha are used[1].

The mechanism of the herbicidal effect and toxicity of paraquat involves the formation of free radical by reduction of the ion and subsequent auto-oxidation to yield the original ion. The free radical itself does not appear to be the primary toxicant but rather hydroxyl radical and/or hydrogen peroxide which is formed during the auto-oxidation of the free radical to the ion as shown in Figure 1.2. The photosynthesis apparatus, light and oxygen are required co-factors for herbicidal action[21,22]. Symptoms of their action include a rapid discoloration and scorch of target leaves, followed by desiccation; chlorosis of unsprayed leaves follows somewhat later[2,23].

### 1.2.3 Photochemical Degradation of Paraquat on Plant Surfaces

In a agricultural application, much of paraquat is

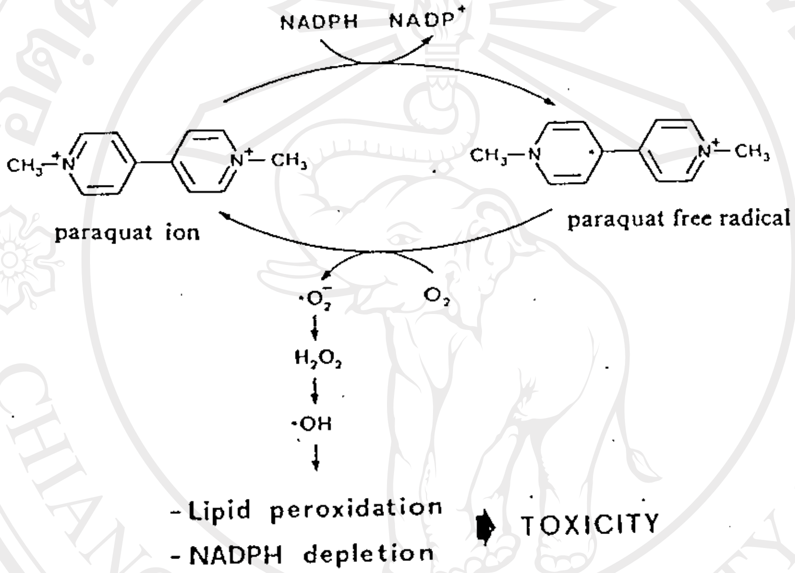

Figure 1.2 Basic mechanism of paraquat toxicity[22].

initially deposited and absorbed on plant surfaces. There have been reports confirming that paraquat can not be metabolized by green plant tissues mainly due to its speed in destroying the photosynthetic tissues which almost certainly result in the destruction of enzyme systems in green parts of plants[1,2]. The greatest loss of paraquat from the surface of treated leaves is due mainly to the photochemical degradation to form 4-carboxyl-1-methyl-pyridylium chloride and methylamine hydrochloride which are less toxic than the parent compound, as shown in Figure 1.3[1]. The rate of this degradation is related to the intensity of ultraviolet radiation between 285-310 nm present in daylight [1,2,24].

### 1.2.4 Toxicity of Paraquat

According to the WHO recommended classification of pesticides by hazard, paraquat belongs to class II, a moderate hazardous substance[25] with an acceptable daily intake (ADI) of 0.004 mg/kg. The oral and dermal toxicity are 150 and 236-500 mg/kg, respectively. The maximum residue limit (MRL) for fruits and vegetables for the European Economic Community is 0.05 mg/kg [5].

### 1.2.5 Evaluation of Risks for Human Health and Effects on the Environment

#### 1.2.5.1 General Population

Residue levels of paraquat in food and drinking water resulting from its normal use, are unlikely to result in the health hazard. This fact is in contrast with the

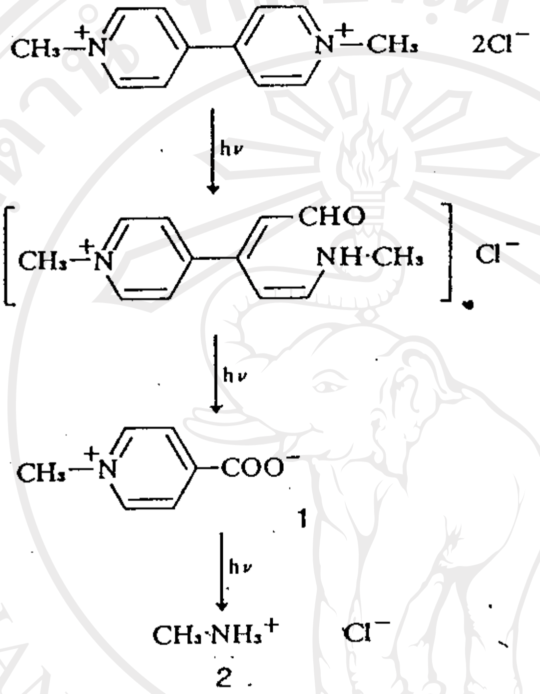

Figure 1.3 Photochemical degradation of paraquat[2]:
(1) 4-carboxyl-1-methyl-pyridylium chloride
(2) Methylamine hydrochloride.

potential serious hazard that may result from handling concentrated paraquat. Accidental paraquat poisoning results mainly from swallowing liquid concentrate that has been decanted into unlabelled bottles or other containers, particularly food and drinking containers that are inappropriately stored[1,14]. Misuse of paraquat as a fermentation activator in the process of illegal alcoholic production once caused serious health problems in Thailand[26].

#### 1.2.5.2 Occupational Exposure

With reasonable work practices, including safety precaution, hygiene measure and proper supervision, occupational exposure during manufacture, formulation and application will not cause hazard. However, the undiluted concentrate must be handled with great care because improper work practices may result in contamination of eyes and skin. Spray concentration should not exceed 5 g of paraquat per liter in order to avoid skin damage and absorption of the paraquat through the skin[1].

#### 1.2.5.3 Environment

Paraquat in soil binds rapidly and tightly to clay minerals and residual phytotoxicity from free-available paraquat is unlikely. It is low toxic to birds. Paraquat shows low toxicity to aquatic organisms under normal condition of use. However, depletion of water oxygen caused by weed decay may pose a problem. In short, paraquat does not seem to represent an environmental hazard under normal condition of use.

### 1.2.6 Analytical Methods

Up to present the analytical method for paraquat in various matrices such as plants, food, environmental and biological materials can be achieved by several acceptable analytical methods. Spectrophotometric method is still one of the official analytical method recommended by U.S.EPA[27]. Current procedures in common use are listed in Table 1.1

## 1.3 Spectrophotometer

Spectrophotometer is the simplest, fastest and least expensive instrument for absorption analysis which provides entirely adequate analytical data for many purposes. This instrument, generally, contains five basic parts, as shown in Figure 1.4[40]. The measurement of absorption of the analyte must follow Beer's law. Up to present, there are several types of double-beam ultraviolet-visible spectrophotometer with high optical and electronic performance to enhance the analytical efficiency.

## 1.4 Solid Phase Extraction (SPE)

Solid phase extraction is a sample preparation technique, introduced in the mid 1970's on the basic concept similar to low pressure liquid chromatography, that utilizes an extraction column containing a small amount of sorbent to extract rapidly and quantitatively specific compounds of interest from a complex sample[15,16]. The SPE is used to

Table 1.1 Analytical methods for paraquat determination.

| Matrix | Analytical procedure | Detection limit | Reference |
|---|---|---|---|
| Soil | Spectrophotometry | 0.01 mg/kg | 1 |
| | Spectrophotometry | - | 1 |
| | Spectrophotometry | 0.5 mg/kg | 1 |
| | GC | 0.01 mg/kg | 1 |
| | GC | 0.01 mg/kg | 1 |
| | Spectrophotometry | 0.05 mg/kg | 26 |
| Water | Spectrophotometry | 0.01 mg/l | 1 |
| | GC | 0.01 mg/l | 1 |
| | GC | 0.01 mg/l | 1 |
| | GC | 0.01 mg/l | 1 |
| | GC | 10 mg/l | 1 |
| | Spectrophotometry | - | 1 |
| | HPLC | 1 ug/kg | 27 |
| | HPLC | 1 ug/ml | 28 |
| | Photokinetics | $1.3\text{x}10^{-6}$M | 29 |
| | Spectrophotometry | 0.001-0.01 mg/l | 30 |
| Air | Spectrophotometry | 0.01 mg/$m^3$ | 1 |
| | GC | 0.5 ng/$m^3$ | 1 |
| Biological materials | Spectrophotometry | 0.01 ug/ml | 1 |
| | Spectrophotometry | 0.01 ug/ml | 1 |
| | Spectrophotometry | 0.01 ug/ml | 1 |
| | GC | 0.03 ug/ml | 1 |
| | GC / MS | 0.025 ug/ml | 1 |
| | RIA | 0.12 ug/ml | 1 |
| | RIA | 0.10 ug/ml | 1 |

Table 1.1 (continued)

| Matrix | Analytical procedure | Detection limit | Reference |
|---|---|---|---|
| Plants | Spectrophotometry | 0.03 mg/l | 31 |
| | Spectrophotometry | 5 ug/ml | 32 |
| | HPLC | 1 ug/ml | 33 |
| | RIA | <0.5 ng | 34 |
| | Spectrophotometry | 0.005 mg/l | 35 |
| | Spectrophotometry | 0.05 ug/ml | 36 |
| | Spectrophotometry | 0.01 mg/kg | 1 |
| | Spectrophotometry | 0.01-1 mg/kg | 1 |
| | GC | 0.01-1 mg/kg | 1 |
| | GC | - | 1 |
| | HPLC | 1 ug/kg | 37 |
| | Spectrophotometry | 0.01-0.05 mg/kg | 38 |

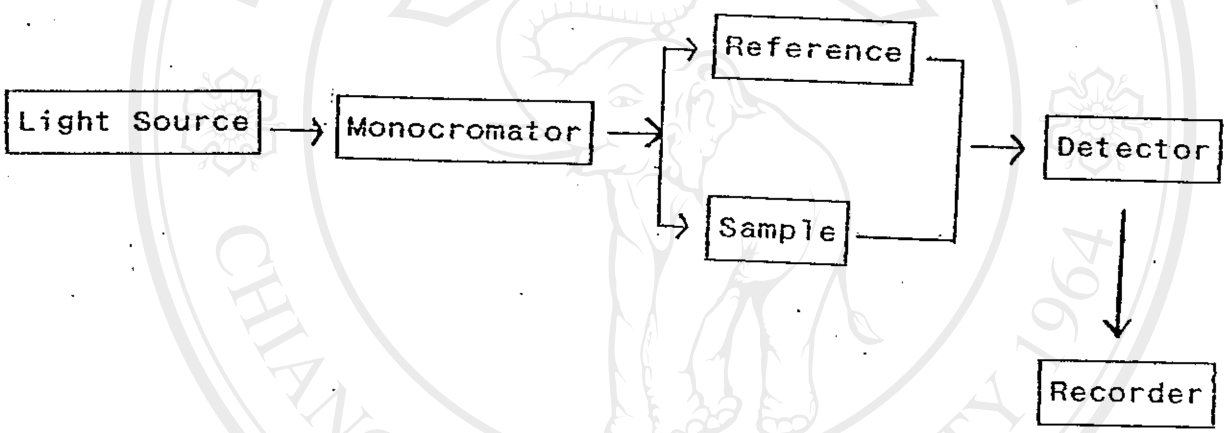

Figure 1.4 Block diagram of a double-beam spectrophotometer[40]

prepare samples prior to analysis by other techniques such as spectrophotometry, high performance liquid chromatography (HPLC), gas chromatography (GC) and radioimmuno assay (RIA), because it provides a clean, concentrated extract which simplifies subsequent analysis by removing interfering or cross-reacting compounds. It is used in a wide variety of applications[18,41]. The process of SPE is illustrated in Figure 1.5 and its advantages are listed in Table 1.2. As most SPE sorbents are derived from bonded silica materials, understanding the properties of bonded silica materials is also very important for developing a reliable extraction method.

Since paraquat is a cationic compound, it is very soluble in the sample matrix, water. Either a very polar or a cation exchange sorbent is required to extract this analyte. The cyano-spe can satisfy this requirement. A solvent with a high ionic strength such as 1.5N hydrochloric acid is used to elute the paraquat[15]. If an aromatic sulfonic acid sorbent is used, complete elution becomes more difficult. And if octadecyl ($C_{18}$) or octyl($C_8$) bonded silica is used, the extraction procedure becomes more complicated[15,42].

## 1.5 Aims and Scope of the Research

The aims of this research were as follows:

1. To determine the amounts of the deposited paraquat on the weeds after application by the farmer's practice and recommended practice.

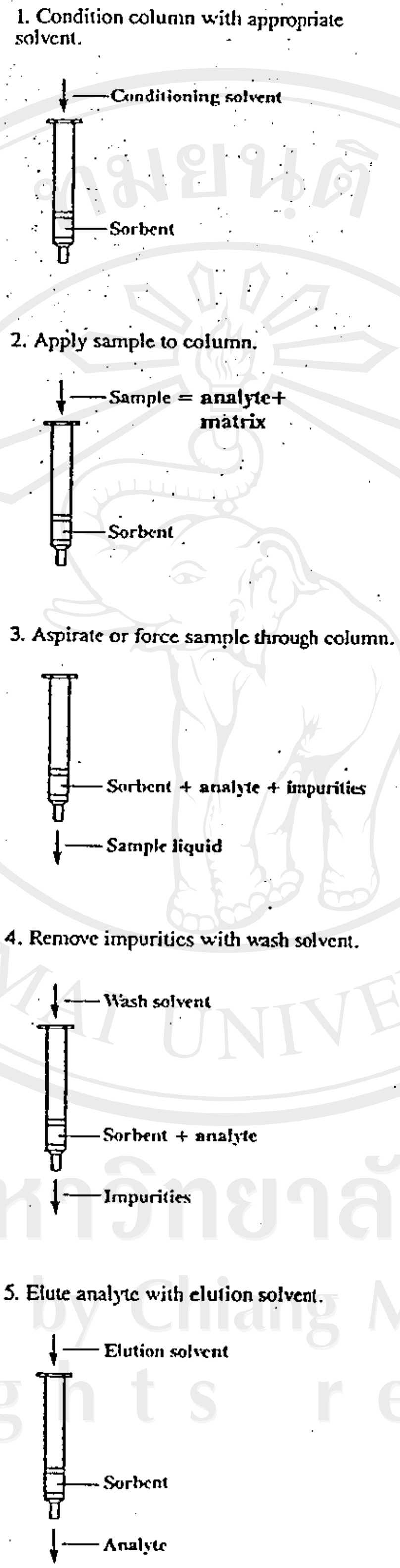

Figure 1.5 Solid phase extraction process[15].

Table 1.2 Solid phase extraction advantages[15].

| | |
|---|---|
| **Rapid** | Approximately six times faster than traditional liquid/liquid extraction. |
| **Efficient** | No emulsions or cross-contamination : purer, drier and higher sample recoveries. |
| **Reproducible** | Estimates most sample handling and transfer for more consistent extractions. Coefficients of variation are typically 2-3%. Save labor, glassware, solvent and ancillary equipment costs. |
| **Safe** | Reduces toxic and flammable solvent use and disposal by 90 %. |

2. To assess the health risk in relation to the use of paraquat in the afore-mentioned application.

The scope of this study was confined to collection of the weed samples from the two trials at the study site after application by the farmer's practice and the recommended practice with subsequent spectrophotometric determinations of the deposited paraquat at the interval of time 0, 1, 2, 3 and 8 days after application.