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# Simple flow injection colorimetric system for determination of paraquat in natural water

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ABSTRACT

A simple and low cost flow injection colorimetric system has been developed for determination of paraquat in natural water. The developed method is based on the reduction of paraquat by using sodium dithionite as a reducing agent in an alkaline medium to produce a blue free radical ion that can be detected by a simple light emitting diode-light dependent resistor (LED-LDR) colorimeter. The standard or sample solution was injected via a set of 3-way solenoid valves into a water carrier stream and flowed to merge with reagent to generate a colored product which is proportional to the concentration of paraquat ion in the solution. Under the optimum condition of the system, i.e., mixing coil length 30 cm, flow rate 2.0 mL $min^{-1}$, sample volume 100 μL, concentrations of dithionite 0.1% (w/v) and sodium hydroxide 0.06 mol $L^{-1}$, a linear calibration graph in the range of 0.2–10.0 mg $L^{-1}$ with a correlation coefficient of 0.9996, and a limit of detection of 0.15 mg $L^{-1}$ were achieved. Relative standard deviation for 9 replicate injections of 1 mg $L^{-1}$ paraquat is 3.7%. A sample throughput of 40 injections $h^{-1}$ was achieved. The limit of detection can be improved by off-line preconcentration of paraquat employing a column packed with Dowex 50WX8-100 (H) cation exchange resin and eluted with 10% (w/v) ammonium chloride in ammonium buffer solution pH 10. The eluting solution was then injected into the FI system for paraquat determination. The proposed system did not suffer from interferences of some possible ions in natural water and other herbicides. Recoveries obtained by spiking 0.5 and 5.0 mg $L^{-1}$ paraquat standard into water samples were in the range of 104–110% and 101–105%, respectively. The developed system can be conveniently applied for screening of paraquat contaminated in natural water.


## 1. Introduction

Pesticides (herbicides, fungicides or insecticides) are environmental pollutants often found in soil, water, atmosphere, and agricultural products, and may exist in harmful levels, posing an environmental threat. Even low levels of contaminants can cause adverse effects on humans, plants, animals and ecosystems [1]. Paraquat (1,1′-dimethyl-4,4′-dipyridinium) is abroad-spectrum herbicide that has been marketed in over 130 countries as a highly effective contact herbicide since 1962. It is very quick-acting herbicide that is absorbed by plants and translocated, thus causing desiccation of the foliage [2,3]. Paraquat is used for a variety of applications including weed control on orchard floors, preplant weed killers for many crops, preharvest desiccants on crops and aquatic weed control [4]. However, it is toxic to human and may cause acute poisoning and even death when ingested in high doses, and it is also known to cause diseases of the liver, lung and heart. It is also toxic to algae, fish, and other aquatic organisms such as crayfish and insects. Thus, it was classified as moderately hazardous. Acute oral $LD_{50}$ (rats) for paraquat (155 mg $kg^{-1}$) is relatively low [2,4]. The 96-h $LC_{50}$ for rainbow trout is 32 mg $L^{-1}$, and 13 mg $L^{-1}$ for brown trout. The $LC_{50}$ for the aquatic invertebrate Daphnia pulex are within 1.2–4.0 mg $L^{-1}$ [5]. The United States Environmental Protection Agency (USEPA) has established maximum contamination level for paraquat in drinking water of 3 μg $L^{-1}$. In Thailand, the Pollution Control Department, Ministry of Natural Resources and Environment (PCD) of Thailand has established maximum concentration allowance for paraquat in water for fresh water animal of 0.5 mg $L^{-1}$ [6]. Because of it has high water solubility and low volatility, after application it can be absorbed by the soil or transported to water by runoff or leaching. It can be easily contaminate in natural water sources and can affect living organisms even human. Therefore, according to all above

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reasons, it is necessary to determine paraquat herbicide residues that contaminated in an environment.

There are several analytical methods have been reported to determine paraquat in various samples (e.g. water, soil, fruit juice, human serum etc.) which comprise high performance liquid chromatography (HPLC) [7–10], electrochemistry [11–14], sensor [15,16], spectrophotometry [17–21], and flow based techniques [19–23]. Chromatography is popular technique to determine paraquat in different samples. It provides high sensitivity and multi-analytes capability. However, this technique employs sophisticated instrument and involves time consuming sample clean-up procedures. Before being analyzed by HPLC, the samples were prepared by solid phase extraction which using graphitized carbon black [7], $C_{18}$ cartridge [9] or silica cartridge [10]. The voltammetric methods have been employed for trace analysis, include square wave voltammetry and differential pulse voltammetry, based on redox reaction that the peak current was found to be directly proportional to the concentration of paraquat. The advantage of voltammetric methods is its fast analysis time due to all samples was used without pre-treatment. Spectrophotometric method is widely used for screening purpose. It is based on the reduction of paraquat by using reducing agents such as sodium dithionite [17,21], sodium borohydride [18], and dehydroascorbic acid [19,20], in an alkaline medium to produce a blue free radical ion which was measured by spectrophotometer. The blue product is not quite stable, so the method is not convenient to use in batchwise manner. Flow injection analysis systems combined with spectrophotometric [19–21] and voltammetric detection [22] has been developed to solve the problem that occurs in batch analysis and provide additional advantages such as improvement of sensitivity, reduction of chemical consumption and analysis time.

In this work, we aim to develop a simple flow injection colorimetric system for screening analysis of paraquat. A low cost light emitting diode-light dependent resistor (LED-LDR) colorimeter was used as a detector instead of an expensive commercial spectrophotometer. A compact FI system was assembled from cost effective devices such as solenoid valves being used instead of injection valve, and a home-made colorimeter with a small data acquisition device. This developed method is inexpensive, simple, fast and low reagent consumption. It was successfully applied to the determination of paraquat in water samples. In addition, a cation exchange preconcentration procedure was developed for improving sensitivity and detection limit of the method.

## 2. Experimental

### 2.1. Apparatus

The manifold of flow injection colorimetric system is depicted in Fig. 1. It consists of a peristaltic pump (Ismatec, Switzerland) with Tygon pump tubings (Cole-Parmer) of 1.14 mm i.d., an injection device assembled from a set of 3-way solenoid valves (Biochemvalve, USA) [24], a flow through cell of 70 µL volume, 10 mm path length and 3 mm window diameter (Highborn,China), a home-made LED-LDR colorimeter with an analog to digital converter (ADC) device (DI-194, DATAQ, USA), and a personal computer for recording a signal as a FI peaks. All the tubing of the system was made of polytetrafluoroethylene (PTFE) (Cole-Parmer), 0.8 mm i.d. A Y-shape connector was used for merging the solution streams. The data evaluation was performed by using the eDAQ chart software (eDAQ, Australia) for integrating the peak heights of the FIA peaks. The circuit of a home-made LED-LDR colorimeter is illustrated in Fig. 2. Red LED was employed as light source and a 5 mm LDR (Senba,China) as light sensor. Resistance of LDR is low in bright light and high in dim light. It is connected in series with a 2 kΩ resistor to act as a voltage divider circuit. The voltage is high in dim light. This voltage is input to operational amplifier (OA) #1 that acts as a zero adjustment circuit. The baseline signal in FIA experiment can be adjusted to zero by a variable resistor (VR) #1. Then, the signal is amplified by OA #2 (by adjusting the VR #2) before feeding into the ADC device.

### 2.2. Reagents, solutions and samples

All chemicals used were of analytical-grade and deionized water (Millipore, Sweden) was used throughout for preparation of solutions.

The chromogenic reagent (R) was freshly prepared by dissolving the 0.1 g of sodium dithionite (Loba, India) and 6 mL of a 1 mol $L^{-1}$ sodium hydroxide solution (Merck, Germany), making the volume up to 100 mL with water, this reagent should not be kept for more than 3 h. Sodium dithionite is unstable in the presence of moisture and should be kept in a desiccator [17]. A 1000 mg $L^{-1}$ Paraquat ($Pq^{2+}$) stock solution was prepared by dissolution of the dichloride salt (Sigma Aldrich, Germany) in water. Working solutions were prepared by dilution of the stock solution with water in the range of 0.2–10.0 mg $L^{-1}$.

Cation exchange resin, Dowex 50W X8-100 (H) (Sigma Aldrich, USA) was used for packing preconcentration column. Saturated sodium chloride solution was prepared by dissolving sodium chloride in deionized water. Eluent was prepared by dissolving 10 g ammonium chloride (QRëC, New Zealand) in 100 mL of 1.3 M ammonium buffer pH 10 solution.

Natural water samples were collected from Ping river, the main river for agricultural activities in Chiang Mai, Thailand. Water from rice field and tap water were also tested. All water samples were kept at the temperature lower than 4 °C and were filtered through a Whatman filter paper (No. 1) before analysis.

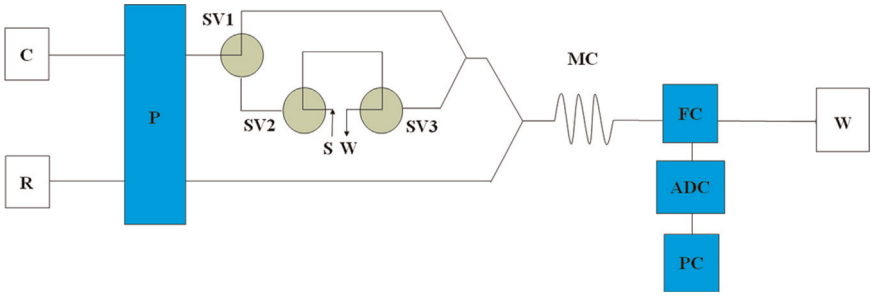


**Fig. 1.** FIA manifold of FI-colorimetric system for determination of paraquat; S=sample/standard paraquat solution, C=carrier ($H_2O$), R=reagent, 0.1% (w/v) sodium dithionite in 0.06 mol $L^{-1}$ NaOH, P=peristaltic pump, SV1-3=3-way solenoid valves, MC=mixing coil, FC=flow cell, ADC=analog to digital converter, PC=personal computer, W= waste.