



# Sequential injection differential pulse voltammetric method based on screen printed carbon electrode modified with carbon nanotube/Nafion for sensitive determination of paraquat



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## ABSTRACT

The screen-printed carbon electrode (SPCE) modified with various nanoparticles has been studied for using as a working electrode in voltammetric technique. The electrochemical behavior of paraquat on different electrodes was studied by cyclic voltammetry (CV), and then differential pulse voltammetry (DPV) has been employed for trace analysis of paraquat based on redox reaction which the peak current was directly proportional to the concentration of paraquat in the solution. The SPCE modified with carbon nanotube dispersed in Nafion and ethanol (SPCE-CNT/Nafion) gave the best result. Sequential injection-differential pulse voltammetric (SI-DPV) method has been developed for more automated analysis and to reduce chemical consumption. The parameters affecting the SI-DPV system such as step potential, modulation amplitude, flow rate, and concentration of sodium chloride as an electrolyte were studied to improve the sensitivity. Under the optimum condition of the system, i.e., Nafion concentration of 1% (w/v), volume of CNT suspension of 2  $\mu\text{L}$ , flow rate of 100  $\mu\text{L s}^{-1}$ , step potential of 5 mV, modulation amplitude of 100 mV and concentration of sodium chloride of 1 M, a linear calibration graph in the range of 0.54–4.30  $\mu\text{M}$  with a good  $R^2$  of 0.9955 and a limit of detection of 0.17  $\mu\text{M}$  (0.03  $\text{mg L}^{-1}$ ) were achieved. The proposed system shows high tolerance to some possible interfering ions in natural water, surfactant, and other pesticides. The relative standard deviation (RSD) was 4.2% for 11 replicate measurements with the same electrode. The reproducibility for the preparation of 7 modified electrodes was 2.3% RSD. Recoveries of the analysis were obtained in the range of 82–106%. The developed system can be conveniently applied for analysis without pretreatment of the samples.

## 1. Introduction

Paraquat (1,1'-dimethyl-4,4'-dipyridinium dichloride) is a herbicide which 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 [1]. The toxicity of paraquat is associated with the reduction of bivalent cation ( $\text{PQ}^{2+}$ ) to a free radical ( $\text{PQ}^{\cdot+}$ ) which reacts with oxygen to form a superoxide radical ( $\text{O}_2^{\cdot-}$ ), hydrogen peroxide ( $\text{H}_2\text{O}_2$ ), and a hydroxyl radical. As these radical are unstable and reactive; they cause lesions in cellular membrane, protein, and DNA [2]. Some health limits which are defined by the EPA at 0.2  $\text{mg L}^{-1}$  is proposed as the drinking water equivalent level, a lifetime exposure concentration protective against adverse, noncancerous health effect that assumes all of the exposure to the

contaminant comes from drinking water [2].

Several analytical methods have been reported for determination of paraquat; they are electrochemistry [3–16], chromatography [17–21], sensor [22,23], spectrophotometry [24–26], and flow based techniques [2,26–29]. However, these techniques employed sophisticated instrument and involved time-consuming sample clean-up procedures except for the electrochemical method which is more convenient method because in most cases sample preparation step was not required. Therefore, the electrochemical methods such as differential pulse and square wave voltammetry have been widely employed for determination of paraquat at trace concentration.

Various supporting electrodes have been modified to improve sensitivity and selectivity in this technique such as glassy carbon electrode (GCE) [3–7], carbon paste electrode (CPE) [8–13], metal

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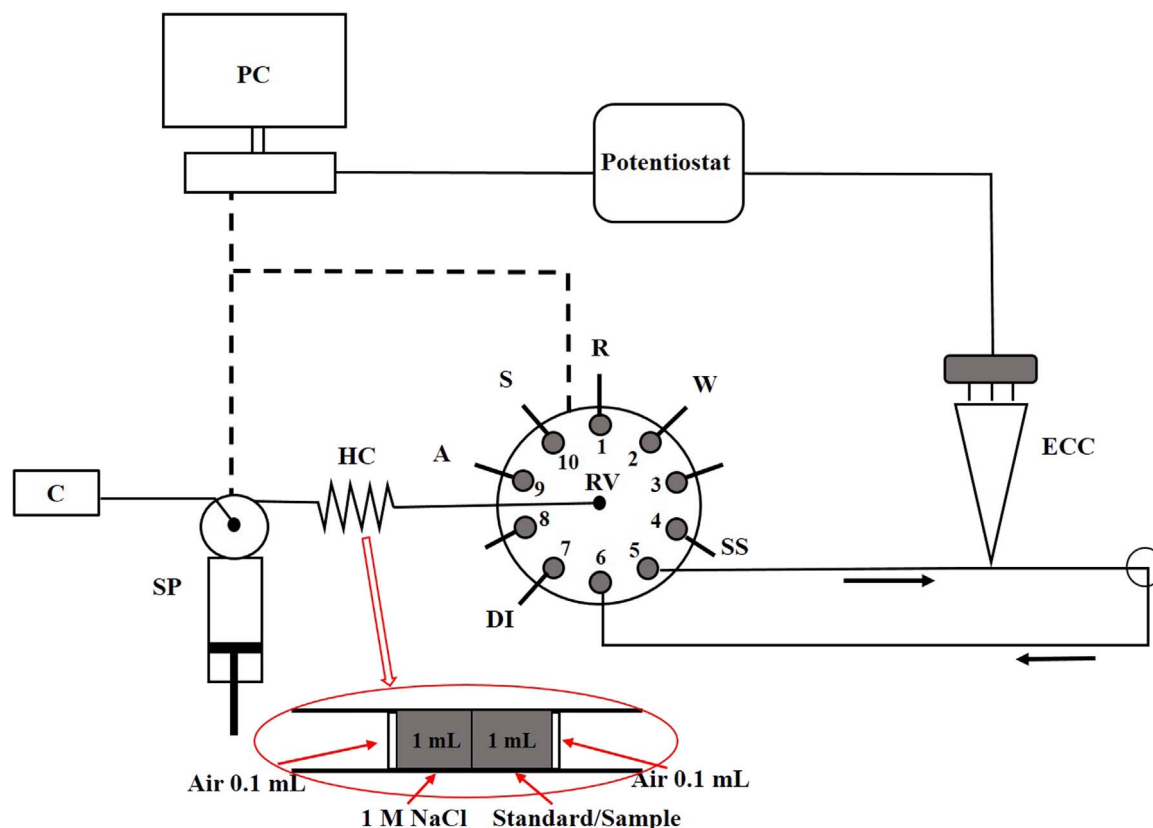
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**Fig. 1.** Manifolds for SI-DPV system for determination of paraquat; A = Air, C = carrier (1 M NaCl), DI = Deionized water, ECC = electrochemical cell, HC = holding coil, PC = Personal computer, S = Standard/Sample, SP = syringe pump, RV = rotary selection valve, R = 1 M NaCl, SS = Saturated NaCl, W = waste.

electrodes (copper, gold, and silver) [14–16], and screen-printed carbon electrodes (SPCE) [30]. Among these SPCE is the most interesting electrode because it can be conveniently fabricated in-house by using a screen-printing machine or by manual hand screen-printing. The SPEs can be easily adapted to detect a wide range of analytes and are inexpensive. In addition, they can be easily combined with other techniques to fit particular applications [31].

Screen printed carbon electrode modified with some nanomaterials have been developed for electrochemical sensor. Reanpang et al. [32] described the modification of palladium nanoparticles (NPs) decorated on carbon nanotube (CNT) on the home-made SPCE for hydrogen peroxide ( $H_2O_2$ ) determination. This modified electrode was incorporated with a home-made flow through cell and applied in a simple flow injection amperometry (FI-Amp). The developed system provided high stability, good repeatability, high sample throughput, and low reagent consumption. Upan et al. [33] have also developed a flow injection amperometric sensor for sensitive and selective determination of hydroquinone. SPCE was modified with CNT, this electrode showed good electron transfer which leads to good sensitivity and reproducibility. Lin et al. [34] have developed a disposable carbon nanotube-based biosensor for the detection of organophosphorus (OP) pesticides and nerve agents. CNTs were modified on SPE and then enzymes were immobilized on the CNTs. The biosensor with acetylcholinesterase/cholineoxidase (AChE/CHO) enzymes provided high sensitivity, wide linear range and low detection limit for analysis of OP compounds.

Carbon nanotubes has good mechanical strength and electrical properties, so it is a suitable material for construction of the electrode. Their excellent electronic properties such as capability of promoting electron transfer and large surface area attract attention for incorporation into composites/modified electrodes for analytical applications [3,32]. Nafion is a polymeric material with cation exchange properties and high mechanical resistance that can act as an effective barrier against surfactant, proteins and humic substances [35], so it is

normally coated on the electrode to improve selectivity. The cationic property of paraquat allows an effective accumulation of this compound onto the Nafion film coated glassy carbon electrode (NFGCE). In this way, good sensitivity and selectivity are achieved by taking the advantages of the preconcentration and surfactants resistant features of Nafion [5].

In this work, we investigate a low cost, easy preparation, and good analytical performance working electrode, based on SPCE modified with various carbon-based nanoparticles. These materials have good electrical conductivity and mechanical strength, as well as being relatively chemically inert in most electrolyte solution, yet retaining a high surface activity and a wide operational potential window [36]. The electrochemical behavior of paraquat on different electrodes was studied by cyclic voltammetry. Then the suitable electrode was selected to use in sequential injection-differential pulse voltammetric (SI-DPV) method for trace analysis of paraquat. It is based on redox reaction that the peak current was found to be directly proportional to the concentration of paraquat. The advantages of voltammetric methods are their high sensitivity and selectivity, fast analysis, and with less or without sample pretreatment [27]. A low detection limit was obtained on the SPCE modified with CNT and Nafion. The SI system help for easy manipulation of various solutions leads to higher automation, which provided advantages in term of fast and simple operation of the method, high sample throughput, and low reagent consumption. Combination of SI with DPV technique provides high sensitivity, precision, and accuracy. The method was applied for determination of paraquat in surface water samples.

## 2. Experiment

### 2.1. Apparatus

The manifold of sequential injection-differential pulse voltammetric

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