

INTEGRATION OF THE FREE LIQUID MEMBRANE INTO ELECTROKINETIC  
SUPERCHARGING - CAPILLARY ELECTROPHORESIS FOR THE  
DETERMINATION OF PARAQUAT AND DIQUAT  
IN ENVIRONMENTAL WATER SAMPLES

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**To my Family**, for their patience, support, love, and for enduring the ups and downs during the completion of this thesis.

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## ABSTRACT

A new approach based on the integration of the free liquid membrane (FLM) into electrokinetic supercharging (EKS) was demonstrated to be a new powerful tool used in order to enhance online preconcentration efficiency in capillary electrophoresis (CE). A small plug of water immiscible organic solvent was used as a membrane interface during the electrokinetic sample injection step in EKS in order to significantly enhance the analyte stacking efficiency. The new online preconcentration strategy was evaluated for the determination of paraquat and diquat present in the environmental water samples. The optimised FLM-EKS conditions employed were as follows: hydrodynamic injection (HI) of 20 mM potassium chloride as leading electrolyte at 50 mbar for 75 s (3% of the total capillary volume) followed by the HI of tris(2-ethylhexyl) phosphate (TEHP) as FLM at a 1 mm length (0.1% of the capillary volume). The sample was injected at 10 kV for 360 s, followed by the HI of 20 mM cetyl trimethylammonium bromide (CTAB) as terminating electrolyte at 50 mbar for 50 s (2% of the total capillary volume). The separation was performed in 12 mM ammonium acetate and 30 mM NaCl containing 20% MeOH at +25 kV with UV detection at 205 nm. Under optimised conditions, the sensitivity was enhanced between 1500- and 1866-fold when compared with the typical HI at 50 mbar for 50 s. The detection limit of the method for paraquat and diquat was 0.15–0.20 ng/mL, with RSDs below 5.5%. Relative recoveries in spiked river water were in the range of 92–100%. A comparison was also made between the proposed approach with sole preconcentration of the field-enhanced sample injection (FASI) and EKS in the absence of the FLM.

## ABSTRAK

Pendekatan baru yang berdasarkan kepada integrasi membran cecair bebas (FLM) dengan superpengecasan elektrokinetik (EKS) telah dibuktikan sebagai kaedah yang sangat berguna untuk meningkatkan keberkesanan prakepekatan dalam talian dalam elektroforesis kapilari (CE). Penyumbat yang terdiri daripada pelarut organik yang tak terlarutkan di dalam air telah digunakan sebagai membran antara muka dalam langkah penyuntikan sampel elektrokinetik ke dalam EKS supaya secara signifikan meningkatkan keberkesanan penindanan analit. Strategi prakepekatan dalam talian yang baru telah dinilai untuk penentuan parakuat dan dikuat di dalam sampel air alam sekitar. Keadaan FLM-EKS optimum yang telah digunakan adalah seperti yang berikut: suntikan hidrodinamik (HI) kalium klorida 20 mM sebagai elektrolit yang utama pada 50 mbar selama 75 saat (3% daripada jumlah keseluruhan isipadu kapilari) dan diikuti dengan HI menggunakan tris (2-etilheksil) fosfat (TEHP) sebagai FLM pada kepanjangan 1 mm (0.1% daripada jumlah isipadu kapilari). Sampel telah disuntik pada 10 kV selama 360 saat, diikuti dengan HI menggunakan setiltrimetilammonium bromida (CTAB) 20 mM sebagai elektrolit penamat pada 50 mbar selama 50 saat (2% daripada jumlah keseluruhan isipadu kapilari). Pemisahan telah dilakukan dalam ammonium asetat 12 mM dan natrium klorida (NaCl) 30 mM yang mengandungi 20% MeOH pada +25 kV dengan pengesanan UV pada 205 nm. Dalam keadaan optimum, kepekaan telah meningkat antara 1500 dan 1866 kali ganda berbanding dengan HI yang biasa pada 50 mbar selama 50 saat. Had pengesanan kaedah ini untuk parakuat dan dikuat adalah antara 0.15 – 0.2 ng/mL, dan RSD kurang daripada 5.5%. Pemulihan relatif sampel air sungai yang ditambah analit adalah dalam julat 92 - 100%. Satu perbandingan turut dilakukan antara pendekatan yang dicadangkan iaitu semata-mata prakepekatan suntikan sampel medan dipertingkatkan (FESI) dan EKS tanpa penglibatan FLM.

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**LIST OF ABBREVIATIONS**

Am-Ac	-	Ammonium Acetate
BGE	-	Background Electrolytes
C <sup>4</sup> D	-	Contactless Conductivity Detector
CGE	-	Capillary Gel Electrophoresis
CTAB	-	Cetyltrimethylammonium Bromide
CZE	-	Capillary Zone Electrophoresis
DI	-	Ultrapure Deionised
DQ	-	Diquat
EE	-	Three-Phase Electroextraction
EKI	-	Electrokinetic Injection
ELISA	-	Enzyme-Linked Immunosorbent Assays
EME	-	Electro-Membrane Extraction
EOF	-	Electro-Osmotic Flow
FASI	-	Field Amplified Sample Injection
FASS	-	Field Amplified Sample Stacking
GC	-	Gas Chromatography
HC-FASS	-	Head Column Field-Amplified Sample Stacking
HCB	-	High Conductivity Buffer
HI	-	Hydrodynamic Injection
HPLC	-	High Performance Liquid Chromatography
KCl	-	Potassium Chloride
LVSS	-	Large Volume Sample Stacking
LE	-	Leading Electrolyte

LOD	-	Limit of Detection
LOQs	-	Limit of Quantitation
LLE	-	Liquid-Liquid Phase Extraction
LPME	-	Liquid-Phase Micro-Extraction
MS	-	Mass Spectrometry
MEKC	-	Micellar Electrokinetic Chromatography
MeOH	-	Methanol
MSS	-	Micelle To Solvent Stacking
NACE	-	Nonaqueous Capillary Electrophoresis
NaCl	-	Sodium Chloride
NaOH	-	Sodium Hydroxide
NPOE	-	2-Nitrophenyl Octyl Ether
PQ	-	Paraquat
PSP	-	Pseudostationary Phase
SEF	-	Sensitivity Enhancement Factor
SDS	-	Sodium Dodecyl Sulfate
SPME	-	Solid-Phase Micro-Extraction
TE	-	Terminating Electrolyte
TEHP	-	Tris(2-Ethylhexyl) Phosphate
tITP	-	Transient Isotachophoresis
$\mu$ -EME	-	Micro-Electromembrane Extraction



**LIST OF SYMBOLS**

<i>k</i>	-	Retention factor
kV	-	Kilovolts
<i>mL</i>	-	Millilitre
<i>ng</i>	-	Nanogram
$r^2$	-	Repeatability
<i>s</i>	-	Seconds

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## **CHAPTER 1**

### **INTRODUCTION**

#### **1.1 Background of Study**

Capillary electrophoresis (CE) is electrophoresis that occurs in a capillary tube [1]. Accomplishments in CE began from the late 1800s. In the experiment, a glass U-tubes and trials of both gel and free solutions was used [2]. According to Arnes Tiselius, in 1930, he successfully shows the ability of electrophoresis by separate of proteins in free solutions [3]. His work went overlooked until the capillaries were introduced by Hjerten proposed in the 1960s. Nonetheless, this technique was not widely recognised until Jorgenson and Lukacs successfully published some papers which showing the ability of CE to employ a capillary in electrophoresis solves some common problems in traditional electrophoresis. For instance, the surface to volume ratio successfully increases by decrease the dimensions of the capillaries, which avoids the problem of overheating by high voltages. The increased efficiency and the remarkable separating capabilities of CE encouraged a raising interest in the scientific community to implement additional growths in the technique.

The online sample preconcentration is a practical method to enhance the concentration sensitivity of the detector by using only a small sample volume requirement in CE. As discussed in several reviews, there are a lot of online sample preconcentration techniques that have been proposed [4-7]. Online sample

preconcentration techniques can easily improve the detection sensitivity of CE when compared with off-line pretreatments. Online sample preconcentration only need to inject a large volume of sample solution alone which means the sample without alteration of the instrument, and the analyte can be focused into a smallest amount of volume inside the capillary.

Besides, recently, the combination of two or more online preconcentration methods has been implemented in various CE applications. The synergistic effect of two or more online preconcentration methods leads to significant enhancements regarding detection sensitivity compared to sole online preconcentration. For example, Hirokawa *et al.* [8] introduced a powerful and noteworthy online preconcentration method featuring the combination of field-amplified sample injection (FASI) and t-ITP, termed electrokinetic supercharging (EKS). In the EKS, analytes are introduced electrokinetically between the leading electrolyte (LE) and the terminating electrolyte (TE) prior to the capillary zone electrophoresis (CZE).

The introduction of a solvent plug prior to sample injection is an ordinary practice in CE analyses. Zhang and Thormann [9] described head column field-amplified sample stacking (HC-FASS), in which a low conductivity solvent plug was introduced prior to the electrokinetic injection (EKI) of the analytes. This method yielded an improved sensitivity enhancement with reproducible results as the analytes introduced into the capillary under the amplified electric field showed rapid stacking at the boundary between the low conductivity solvent plug and the running buffer.

Later, Kubáň and Boček [10, 11] reported an interesting integration of the immiscible organic solvent plug, described as a FLM into a micro-electromembrane extraction ( $\mu$ -EME) approach. The FLM acts as a selective phase interface between the aqueous donor and the acceptor solution and facilitates the electrically induced transfer of charged species in the transparent tubing. This offline three-phase extraction showed feasibility in efficiently retreating samples with complex matrices, e.g. high concentrations of salts and

proteins and allowing the resulting acceptor solutions to be analyzed directly using CE techniques. Various applications, including the quantification of basic drugs in undiluted biological samples [10], as well as perchlorate in drinking water samples [12], were successfully implemented. In the present work, the unique features of FLM were adopted and directly integrated into the existing EKS method in order to further enhance the detection sensitivity in CE.

On the other hand, the herbicides were used aggressively in agriculture will caused a serious health risks and hazards in animal and human life. Some herbicides are unrelenting organic pollutants. Hence, they will be absorbed into the soil and accumulate in the trophic food chain. However, the use of herbicides is important in modern agricultural production in order to control weeds.

Paraquat (PQ) and diquat (DQ) are toxins and often cause poisoning [13]. Hence, these two herbicides are on the priority list of pesticides for a monitoring program in the USA's national pesticide survey. Quats can be detected in water, soil and biological samples. However, due to the low concentration of analytes in environmental and biological samples, a preconcentration step is necessary before the samples can be detected using capillary zone electrophoresis. According to the United States Environmental Protection Agency, the maximum contaminant level is 3 ppb of paraquat and 20 ppb of diquat [14].

## **1.2 Problem Statement**

The determination of paraquat and diquat using CE coupling with various offline preconcentration techniques has been focused on recently. However, to the best of our knowledge, there is still no single step high sensitivity "sample-to-answer" analysis protocol available. The use of herbicides is important in modern agricultural production in order to control weeds. Due to the low concentration of herbicides present in environmental water samples, a preconcentration method is needed before these analytes can be detected by CE. Many of the existing

preconcentration methods are carried out offline in order to reduce systematic mistakes. Nevertheless, these procedures are normally tedious and time-consuming. Therefore, a new analytical approach that combines a preconcentration method with CE is desired that allows for the direct analysis of environmental water samples without the need of any sample pretreatment step.

### **1.3 Objectives**

The objectives of this study are:

1. To evaluate the performance of conventional preconcentration techniques coupled with CE in determining paraquat and diquat levels in river water samples.
2. To develop and investigate the performance of a new online preconcentration technique by introducing an FLM plug into the existing EKS method coupled to CE for the determination of paraquat and diquat in river water samples.
3. To validate and compare the newly established FLM-EKS-CE technique with conventional online preconcentration techniques for the determination of paraquat and diquat in river water samples.

### **1.4 Scopes of Study**

In this study, a new direct coupling of a EKS technique with the unique feature of an FLM to capillary zone electrophoresis was demonstrated to determine cationic herbicides in environmental water. Several important parameters, including background electrolyte concentration, injection mode and the effect of separation length were optimized and thoroughly investigated using conventional CE instrumentation.

Buffer system optimization to separate the targeted herbicides using the conventional CE method was carried out by testing different buffer concentrations.

Additionally, the FASI optimization parameters such as the injection time and injection voltage were investigated. EKS optimization, such as the type of leading electrolyte (LE) and terminating electrolyte (TE), the plug length of the LE and TE and the sample injection time were tested. For the EKS-FLM technique, the type of FLM, the plug length of the FLM and the drawbacks of FLM were investigated. Finally, the new method was validated and subsequently applied to the rapid determination of environmental water samples.

### **1.5 Significance of Study**

Paraquat and diquat are extensively used as agricultural herbicides to manage the weeds of crop and aquatic. Hence, the pollution of drinking and environmental water with paraquat and diquat was trusted as a risk for liver, heart, lung and kidney diseases [15]. Besides, diquat and paraquat are poisonous to algae, fish and other aquatic organisms such as crayfish and insects. When humans consume these foods, this might have negative effects on the human body.

The aim of this work was to develop a rapid and cost-effective method for the rapid and direct determination of paraquat and diquat using CE with integration of the unique features of FLM with EKS to further enhance the detection sensitivity of PQ and DQ, which are normally present at ultra-trace levels in environmental water samples. This will significantly improve the safety of our agricultural products and ensure the high quality of the water supply for all people, and subsequently improve the quality of health among inhabitants. This study is also expected to create a new sample-to-answer analytical approach without any offline sample pretreatment steps, which can be directly employed for a wider range of applications including food and pharmaceutical analysis.

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