

ON-LINE PRE-CONCENTRATION OF ARSENIC COMPOUNDS BY DYNAMIC  
pH JUNCTION-CAPILLARY ELECTROPHORESIS

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This thesis is dedicated to the memories of my beloved late father and mother

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## ABSTRACT

Capillary electrophoresis (CE) with ultraviolet (UV) detection suffers from a poor concentration sensitivity resulting in a significant obstacle for analysis of part per billion levels of analytes in real samples. Therefore, there is a need to develop a simple yet effective pre-concentration method to enhance concentration sensitivity of trace level analytes in real samples for CE analysis. In this research, dynamic pH junction as an on-line pre-concentration method was employed for the determination of the animal feed additive roxarsone (3-nitro-4-hydroxyphenylarsonic acid) and four of its most possible degradation products (arsenite, arsenate, monomethylarsonic acid and dimethylarsinic acid). Phenylarsonic acid was included as an internal standard. The separation was conducted in a fused-silica capillary using 15 mM Na<sub>2</sub>HPO<sub>4</sub>-Na<sub>3</sub>PO<sub>4</sub> buffer, pH 10.6 and 15 mM CH<sub>3</sub>COOH, pH 3.5 sample matrix at a voltage of 25 kV. Arsenite, arsenate, monomethylarsonic acid and dimethylarsinic acid were detected at 192 nm wavelength while phenylarsonic acid and roxarsone were detected at 254 nm wavelength. This on-line pre-concentration method, compared to the conventional capillary zone electrophoresis (CZE) method, resulted in an increased detection response of up to 51-fold in terms of peak height of arsenic compounds. The lower limit of detections (LODs) for the arsenic compounds obtained were in the range of 0.34-1.93 µg/L in comparison with conventional capillary zone electrophoresis with the LODs in the range of 140-293 µg/L. Reproducibility of the analytes in terms of migration time was in the range of 1.96-5.37% RSD. The proposed method was applied to the determination of roxarsone in chicken manure and soil samples. Roxarsone was extracted with distilled water and the analyte was then cleaned up using solid-phase extraction technique which uses a high anion exchange cartridge (HAX) as an off-line sample pre-concentration and sample clean up as well as C<sub>18</sub> cartridge for further sample clean up mainly to remove organic contaminant before analysis using dynamic pH junction-CE. Recovery of the roxarsone obtained was 70 ± 1% for chicken manure samples and 72 ± 2% for soil samples.

## ABSTRAK

Elektroforesis rerambut (CE) dengan pengesan ultralembayung (UV) mempunyai kelemahan disebabkan kepekaan yang rendah terhadap kepekatan mengakibatkan halangan yang jelas bagi analisis pada tahap bahagian per billion kepekatan analit dalam sampel sebenar. Oleh itu, adalah perlu untuk membangun kaedah pra-pemekatan yang ringkas tetapi berkesan dalam meningkatkan kepekaan terhadap kepekatan analit yang rendah dalam sampel sebenar bagi analisis CE. Dalam penyelidikan ini, titian pH dinamik telah dipilih sebagai kaedah pra-pemekatan talian terus bagi penentuan makanan tambahan haiwan, roksarson (asid 3-nitro-4-hidroksifenilarsonik) dan empat hasil produk degradasi (arsenit, arsenat, asid monometilarsonik dan asid dimetilarsinik) yang paling mungkin. Asid fenilarsonik turut dimasukkan sebagai piawai dalaman. Pemisahan telah dijalankan di dalam turus rerambut silika menggunakan larutan penimbal 15 mM  $\text{Na}_2\text{HPO}_4\text{-Na}_3\text{PO}_4$ , pH 10.6 dan sampel matrik 15 mM  $\text{CH}_3\text{COOH}$ , pH 3.5 pada keupayaan 25 kV. Spesies arsenik tak organik dikesan pada 192 nm sementara spesies arsenik organik dikesan pada 254 nm. Kaedah pra-pemekatan talian terus ini menghasilkan peningkatan respons pengesanan sehingga 51-kali ganda terhadap ketinggian puncak sebatian arsenik berbanding kaedah elektroforesis zon rerambut konvensional (CZE). Had pengesanan yang rendah terhadap enam sebatian arsenik yang diperolehi berada dalam julat 0.34-1.93  $\mu\text{g/L}$  berbanding dengan had pengesanan elektroforesis zon rerambut konvensional yang berada dalam julat 140-293  $\mu\text{g/L}$ . Kebolehulangan analit terhadap masa dalam julat 1.96-5.37% RSD. Kaedah yang telah dicadangkan ini telah diaplikasikan bagi penentuan roksarson dalam sampel tahi ayam dan sampel tanah. Roksarson diekstrak menggunakan kaedah pengekstrakan larut air dan analit kemudiannya dibersihkan menggunakan teknik pengekstrakan fasa pepejal menggunakan kartrij penukaran anion tinggi (HAX) yang berfungsi untuk pra-pemekatan sampel secara talian tidak terus dan untuk membersihkan sampel dan kartrij  $\text{C}_{18}$  untuk membersihkan lagi sampel terutamanya dalam penyingkiran bahan pencemar organik sebelum dianalisis oleh titian pH dinamik-CE. Nilai perolehan semula bagi roksarson ialah  $70 \pm 1\%$  bagi sampel tahi ayam sementara  $72 \pm 2\%$  ialah nilai perolehan semula roksarson yang diperolehi bagi sampel tanah.

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**LIST OF SYMBOLS**

cm	-	Centimeter
°C	-	Degree Celsius
g	-	Gram
g/mol	-	Gram per mol
kg	-	Kilogram
kg/L	-	Kilogram per Liter
kV	-	Kilo Volt
M	-	Molar
MΩ	-	Milli Ohm
mbar	-	Milli Bar
mA	-	Milli Ampere Unit
min	-	Minute
mL	-	Milli Liter
mM	-	Milli Molar
N	-	Separation efficiency
nL	-	Nano Liter
nm	-	Nano Meter
ppm	-	Parts per Million
ppb	-	Parts per Billion
$r^2$	-	Correlation coefficient
s	-	Second
t	-	Migration time
$\mu_{app}$	-	Electrophoretic mobility at the apparent charge of the analyte
$\mu_{EOF}$	-	Electroosmotic flow mobility

$\mu_{EP}$	-	Electrophoretic mobility
$\mu\text{m}$	-	Micro Meter
$\mu\text{L}$	-	Micro Liter
$v$	-	Electrophoretic velocity
$v_{EOF}$	-	Electroosmotic flow velocity

**LIST OF ABBREVIATIONS**

AAS	-	Atomic absorption spectrometry
AFS	-	Atomic fluorescence spectrometry
ASV	-	Anodic stripping voltammetry
As(III)	-	Arsenite
As(V)	-	Arsenate
BNFs	-	Band narrowing factors
BGE	-	Background electrolyte
CSV	-	Cathodic stripping voltammetry
CE	-	Capillary electrophoresis
CEC	-	Capillary electrochromatography
CGE	-	Capillary gel electrophoresis
CIEF	-	Capillary isoelectric focusing
CITP	-	Capillary isotachopheresis
CTAC	-	Cetyltrimethylammonium chloride
CZE	-	Capillary zone electrophoresis
DPASV	-	Differential pulse anodic stripping voltammetry
DPCSV	-	Differential pulse cathodic stripping voltammetry
DIBR	-	Detector to injection band width ratio
DMA	-	Dimethylarsinic acid
EOF	-	Electroosmotic flow
FASI	-	Field amplified sample injection
FSCE	-	Free solution capillary electrophoresis
HAX	-	High anion exchange
HG	-	Hydride generation

HG-AAS	-	Hydride generation atomic absorption spectrometry
HPLC	-	High performance liquid chromatography
ICP-AES	-	Inductively coupled plasma-atomic emission spectrometry
ICP-MS	-	Inductively coupled plasma-mass spectrometry
LV-FASI-CZE	-	Large volume field amplified stacking injection capillary zone electrophoresis
LODs	-	Limit of detections
MMA	-	Monomethylarsonic acid
MEKC	-	Micellar electrokinetic capillary chromatography
3-NHPAA	-	3-nitro-4-hydroxyphenylarsonic acid
PAA	-	Phenylarsonic acid
PDDAC	-	Poly(diallyldimethylammonium chloride)
RSD	-	Relative standard deviation
SEF <sub>height</sub>	-	Sensitivity enhancement factor in terms of peak height
SPE	-	Solid phase extraction
t-ITP	-	Transient isotachopheresis
UV	-	Ultra Violet
UV/VIS	-	Ultra Violet / Visible
V-DIF	-	Velocity-difference induced focusing

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## CHAPTER 1

### INTRODUCTION

#### 1.1 Problem Statement and the Need of Study

3-nitro-4-hydroxyphenylarsonic acid (3-NHPAA or roxarsone) is an anthropogenic organoarsenic compound that is widely used as an additive in the poultry industry to control coccidial intestinal parasites, improve feed efficiency and enhance weight gain for better production of poultry. This food supplement does not accumulate in the tissue or feathers of chicken but is believed to be excreted unchanged in poultry litter. Normally, the waste from poultry litter is applied to nearby crop land as fertilizer to reduce the cost of transporting the litter. Once in the agricultural field, roxarsone degrades rapidly into a more mobile and toxic arsenic species and thus providing the sources for arsenic contamination of surface and groundwater (Garbarino *et al.*, 2001). Of the various sources of arsenic exposure to human health, drinking water that is derived from surface waters (rivers, lakes, reservoirs and ponds) and groundwater is the major source for human exposure to arsenic. Therefore, it is very important to study this organoarsenic compound and its transformation products for the determination and identification of these arsenic compounds in real environmental samples.

For the measurement of trace level of roxarsone and its degradation products, various methods have been developed such as hydride generation atomic absorption spectrometry, HG-AAS (Gonzalez *et al.*, 2003; Maiti *et al.*, 2004; Bortoleto *et al.*, 2005 and Anthemidis *et al.*, 2005), voltammetry (Greulach and Henze, 1995; Sun *et*

*al.*, 1997 and Kopanica and Novotny, 1998; Profumo *et al.*, 2005), high performance liquid chromatography, HPLC (Martin *et al.*, 1995; Stummeyer *et al.*, 1996 and Gomez *et al.*, 1997), inductively coupled plasma mass spectrometry, ICP-MS (Wangkarn and Pergantis, 1999; Jackson *et al.*, 2003; Niemela *et al.*, 2003; Yu *et al.*, 2003; Bednar *et al.*, 2004 and Zhang *et al.*, 2004). and capillary electrophoresis, CE (Lopez-Sanchez *et al.*, 1994; Van den Broeck and Vandecasteele, 1998; Greschonig *et al.*, 1998; Sun *et al.*, 2002 and Chen *et al.*, 2003).

In this research, CE has been chosen for the separation and determination of arsenic species because CE has the advantages of short analysis time, high separation efficiency, lower solvent consumption, small sample size and low operating costs compared to other techniques that have been favored such as HPLC and ICP-MS which are more expensive and more complex in their instrumentation.

Capillary electrophoresis (CE) is an evolution of traditional slab gel electrophoretic technique. All commercially available CE is usually equipped with UV/VIS detector due to its ease of operation. However, CE suffers from the poor concentration sensitivity when using UV detection because of the small injection volume and short optical path length (Simonet *et al.*, 2003). As a result, CE is often not suitable for the analysis of real environmental samples. Some efforts have been attempted to improve the detection sensitivity of CE including the use of Z-cells or bubble cells to extend the optical path length (Mainka and Bachmann, 1997), the use of highly sensitive detection methods such as laser-induced fluorescence (Chen *et al.*, 2003) sample enrichment via off-line solid phase extraction method (Rao *et al.*, 1999) and the use of on-line pre-concentration techniques (Zhang *et al.*, 2001 and Britz-McKibbin *et al.*, 2002). On-line pre-concentration technique is simple and do not require modification to the existing instrument, since electrophoretic focusing of analytes is effected within the same capillary used for separation and useful for sensitivity enhancement.

In general, on-line pre-concentration methods consist of four techniques; sample stacking, sweeping, transient isotachoporesis and dynamic pH junction (Lin and Kaneta, 2004). Among these techniques, dynamic pH junction was selected as an

on-line pre-concentration technique in this study because the focusing procedure of dynamic pH junction is easy to perform since it does not require coating of the capillary or the use of polarity switching, as it often necessary for large volume sample stacking (Zhang *et al.*, 2001). To our knowledge, there has been no report on focusing of arsenic compounds using on-line pre-concentration method based on the dynamic pH junction.

## 1.2 Objectives of Research

The optimum experimental conditions for simultaneous separation of arsenic compounds which consists of arsenite; As(III), arsenate; As(V), monomethylarsonic acid; MMA, dimethylarsinic acid; DMA, and 3-nitro-4-hydroxyphenylarsonic acid; roxarsone and phenylarsonic acid; PAA using CZE will be determined. Experimental parameters such as the type of buffer, pH of buffer solution, separation voltage and detection wavelengths were investigated.

An on-line pre-concentration technique using the dynamic pH junction-CE will be developed to increase the detection sensitivity of the arsenic compounds. The factors included in the optimization scheme are buffer pH, pH of the sample matrix, concentration of the sample matrix and injection lengths.

The percentage recoveries of spiked soil and chicken manure samples upon application of the dynamic pH junction method as an on-line pre-concentration method combined with the well developed solid phase extraction (SPE) method will be determined. SPE method is employed for the purpose of sample clean-up as well as an off-line sample pre-concentration. Two types of SPE cartridges were used, that is C<sub>18</sub> cartridge for sample clean up mainly to remove organic contaminant and HAX (high anion exchange) cartridge for the purpose of sample pre-concentration.

### 1.3 Scope of Research

Arsenic compounds i.e. arsenite; As(III), arsenate; As(V), monomethylarsonic acid; MMA, dimethylarsinic acid; DMA, 3-nitro-4-hydroxyphenylarsonic acid; roxarsone and phenylarsonic acid; PAA were determined using CE. These arsenic compounds were chosen because these compounds are the most probable degradation products of roxarsone while PAA serve as an internal standard. For the purpose of increasing the detection limit of these five arsenic compounds when using CE, the on-line pre-concentration method based on dynamic pH junction was used. Increasing the sensitivity is important for the analysis of trace level of arsenic compounds in environmental samples. The limit of detection (LOD) for these five arsenic compounds using dynamic pH junction and normal CZE mode were compared. The dynamic pH junction method was applied to spiked soil samples and spiked litter samples. In the case of spiked samples, the samples were passed through C<sub>18</sub> cartridge to remove the organic contaminant and the samples were further pre-concentrated using HAX (high anion exchange) cartridge prior to analysis by CE.

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