

SEPARATION OF ORGANOPHOSPHORUS PESTICIDES USING MICELLAR
ELECTROKINETIC CHROMATOGRAPHY

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

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ABSTRACT

This study was undertaken to separate hydrophobic and hydrophilic organophosphorus pesticides (OPPs) using micellar electrokinetic chromatography (MEKC) with on-column UV detection and the challenge of decreasing the limit of detections (LODs) was tried to meet by online concentration methods. The influence of separation buffer and sample matrices were investigated with respect to migration, efficiencies, peak shapes and resolution. Successful separation of hydrophobic OPPs (methidathion, diazinon, quinalphos, chlorpyrifos and profenofos) was achieved by normal mode MEKC with sodium dodecyl sulphate, SDS (NM-MEKC-SDS) that comprised a separation buffer of 10 mM phosphate-borate (pH 9.3), 10 mM SDS and 10 % v/v 1:1 mixture of methanol-acetonitrile, where sample was prepared in similar buffer matrix and injected electrokinetically. An alternative approach is proposed to predict the retention factors (k), on the basis of a functional relationship between solutes retention and separation potentials. Using online concentration technique (sweeping-NM-MEKC-SDS), sensitivity enhancement factors (SEF_{area} and SEF_{height}) were found to be 10 for each pesticide. Sensitivity enhancement was improved further for diazinon, quinalphos and profenofos (LODs in sub-ppm range) by increasing the sample plug length. Hydrophilic OPPs (phosphamidon, dicrotophos and monocrotophos) were successfully separated in both basic and acidic phosphate buffer. At least 100-fold improvement in detector response was achieved by stacking in reverse migrating micelles (SRMM) that corroborated the LODs in sub-ppm level, and those levels were found detectable by spiking in a natural water sample. The methods developed here, sweeping-NM-MEKC-SDS for hydrophobic OPPs and SRMM for hydrophilic OPPs are expected to be useful either by direct injecting the sample upon filtration or with prior suitable offline sample enrichment steps depending on the contaminant level.

ABSTRAK

Kajian ini dijalankan untuk memisahkan pestisid organofosforus (OPPs) hidrofobik dan hidrofilik dengan kromatografi elektrokinetik misel (MEKC) dengan pengesanan ultralembayung pada turus dan cabaran untuk merendahkan had pengesanan (LODs) telah dipenuhi melalui kaedah kepekatan talian terus. Pengaruh penimbal pemisahan dan matriks sampel telah dikaji terhadap migrasi, kecekapan, bentuk puncak dan resolusi. Pemisahan OPPs hidrofobik (metidation, diazinon, kuinalfos, klorpirifos dan profenofos) berjaya dilakukan dengan mod normal MEKC menggunakan natrium dodesil sulfat, SDS (NM-MEKC-SDS) yang mengandungi penimbal pemisahan 10 mM fosfat-borat (pH 9.3), 10 mM SDS dan 10 % v/v 1:1 campuran metanol-asetonitril dengan sampel disediakan dalam matriks penimbal yang sama dan disuntik secara elektrokinetik. Suatu pendekatan alternatif telah dicadangkan untuk meramal faktor penahanan (k) berdasarkan hubungan berfungsi antara penahanan zat terlarut dan keupayaan pemisahan. Dengan menggunakan teknik kepekatan talian terus (sapuan-NM-MEKC-SDS), faktor peningkatan kepekaan (SEF_{luas} dan $SEF_{\text{ketinggian}}$) sebanyak 10 bagi setiap pestisid (sapuan NM-MEKC-SDS). Peningkatan kepekaan selanjutnya diperoleh untuk diazinon, kuinalfos dan profenofos (LODs dalam julat sub-ppm) dengan menambahkan panjang sampel penyumbat (sample plug). OPPs hidrofilik (fosfamidon, dikrotofos dan monokrotofos) telah berjaya dipisahkan dalam kedua-dua penimbal fosfat berbes dan berasid. Sekurang-kurangnya 100-kali ganda peningkatan respon pengesanan telah dicapai dengan kaedah himpunan (stacking) misel migrasi terbalik (SRMM) dan disokong oleh LOD dalam aras sub-ppm dan aras ini didapati dapat dikesan dalam sampel air semula jadi pakuan. Kaedah yang dibangunkan ini, sapuan-NM-MEKC-SDS untuk OPPs hidrofobik dan SRMM untuk OPPs hidrofilik dijangkakan berguna sama ada secara suntikan terus sampel terus selepas penurasan atau dengan kaedah prapemekatan talian luar bergantung aras pencemar.

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LIST OF SYMBOLS

μA	-	Micro ampere
μ_{eo}	-	Electroosmotic mobility
μ_{ep}	-	Electrophoretic mobility
μL	-	Micro liter
cm	-	Centimeter
k	-	Retention factor (capacity factor)
K	-	Distribution coefficient
K_{ow}	-	Octanol/Water partition coefficient
kPa	-	Kilo Pascal
L	-	Liter
min	-	Minute
mL	-	Mili Liter
mM	-	Mili Molar
N	-	Efficiency
nL	-	Nano Liter
nm	-	Nano Meter
R_s	-	Resolution
s	-	Seconds
S_w	-	Water solubility
t_0	-	Migration time EOF marker
t_m	-	Migration time micelle marker
V	-	Voltage
v_{eo}	-	Electroosmotic velocity
v_{ep}	-	Electrophoretic velocity
ζ	-	diffused double layer potential
κ	-	Number of regression lines

LIST OF ABBREVIATIONS

AcN	-	Acetonitrile
BBMA	-	Butyl acrylate-butyl methacrylate-methacrylic acid
BGE	-	Background electrolyte
BMHC	-	Buffer matrix higher concentration
BMLC	-	Buffer matrix lower concentration
Bor	-	Borate
bp	-	Boiling point
CD	-	Cyclodextrin
CE	-	Capillary electrophoresis
CGE	-	Capillary gel electrophoresis
Ch	-	Chlorpyrifos
CL	-	Confidence Limit
CMC	-	Critical micelle concentration
CZE	-	Capillary zone electrophoresis
DD	-	Distilled deionized
DF	-	Degree of Freedom
Dz	-	Diazinon
EC	-	Electro chromatography
EKC	-	Electrokinetic chromatography
EOF	-	Electro osmotic flow
FESI	-	Field enhanced sample injection
GC	-	Gas chromatography
HB	-	Hydrogen bond
HPLC	-	High performance liquid chromatography
ID	-	Internal diameter
IEF	-	Isoelectric focusing (CE)

ITP	-	Isotachophoresis (CE)
LC	-	Liquid chromatography
LIF	-	Laser-induced fluorescence
LSER	-	Linear solvation energy relationship
Me	-	Methanol
MEKC	-	Micellar electrokinetic chromatography
mp	-	Melting point
MRL	-	Maximum residue levels
MS	-	Mass spectrometry
Mt	-	Methidathion
MT	-	Metric Ton
MW	-	Molecular weight
NAHC	-	Nonaqueous higher concentration
NM	-	Normal mode
NSM	-	Normal stacking mode
OD	-	Outer diameter
OPPs	-	Organophosphorus pesticides
Ph	-	Phosphate
Pr	-	Profenofos
PS	-	Pseudostationary phase
PTFE	-	Polytetrafluorethane
Qu	-	Quinalphos
RM	-	Reverse mode
SC	-	Sodium Cholate
SDS	-	Sodium dodecyl sulphate
SEF	-	Sensitivity enhancement factor
SRMM	-	Stacking reverse migrating micelles
SS	-	Sum of Squares
UTM	-	Universiti Teknologi Malaysia
UV	-	Ultraviolet
VIS	-	Visible

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CHAPTER 1

SUMMARY OF THESIS

1.1 Background

Since the first introduction exactly two decades ago, micellar electrokinetic chromatography (MEKC) has been widely adopted as a separation technique in hundreds of different applications. MEKC is a mode of capillary electrophoresis (CE) that is capable of separating ionic and neutral compounds in a single electrophoretic run. MEKC involves a pseudostationary phase (i.e. micelles) into the separation buffer and uses the same instrumental setup as CE. Electrophoretic migration of neutral compounds are based on their degree of interaction with the charged micelles and electroosmotic flow (EOF), therefore, separation of neutral compounds in MEKC is directly related to the differences in the interactions between micelles and compounds.

To date, separation of organophosphorus pesticides (OPPs) by MEKC methods are virtually scarce. However in the few available MEKC works for the separation of various pesticides, only qualitative aspects of the separation were focused. The strong hydrophobic nature of OPPs might have resulted a strong interactions with the micelles which could pose a real difficulties to separate them in MEKC if the separation buffer is not critically optimized. On the other hand, all proposed online concentration methods compatible for MEKC are quite new. Therefore in this study, attempts were made to separate a number of hydrophobic

and hydrophilic OPPs by optimised MEKC methods and suitable online concentration techniques were used to achieve a lower limit of detections (LODs).

1.2 Summary

Only chromophoric OPPs were selected and classified into hydrophobic and hydrophilic groups due to the specific detection tool (UV absorption), their different sensitivity in single wavelength detection and their characteristic behaviour in buffer and sample matrices.

Besides a concise introduction with objectives of this work in Chapter 2, and general experimental in Chapter 3, this thesis contains 4 more chapters (Chapter 4, 5, 6 and 7) illustrating the basic optimization feature, separation performances, necessary discussions, conclusions and the future scope of MEKC in separation analysis. Chapter 4 represents the key aspects of optimization of several constituents in separation buffer viz. surfactant, buffer, organic solvents, and cyclodextrin (CD) as well as other experimental conditions by emphasizing the qualitative aspects of the separation, affected by the investigating variables. Chapters 5 and 6 provide the actual methods for practical use and the utility of the methods are considered through the quantitative viewpoint. However, it should be made clear that the foundations of developed methods of Chapter 5 and 6 lie in Chapter 4, therefore, methodological information may be felt inadequate in those chapters but can be retrieved if it is read in congruence with Chapter 4.

In Chapter 4, stepwise optimizations of the levels of phosphate and borate buffer, SDS surfactant, methanol, acetonitrile, 2-propanol as modifiers with other related experimental factors (e.g., sample matrix, sample injection mode, detection wavelength) were tried in the separation of hydrophobic OPPs (methidathion, diazinon, quinalphos chlorpyrifos and profenofos). 10 mM SDS surfactant, a little over its critical micelle concentration (CMC) value (~ 8 mM), was found optimum in these conditions. Phosphate buffer was found to be effective buffer but addition of borate buffer would give some advantages in the sensitivity and baseline stability,

therefore, separation in mixed buffers (10 mM of 1:1 phosphate and borate) was found better in terms of peak shapes, while lacking the full support of statistical comparison tests. Similarly, methanol was found to be the most favourable organic solvent that can be used as a modifier in separation buffer and without addition of methanol peaks would not be obtained with appreciable range of efficiency. The addition of certain proportion of acetonitrile with methanol (10 % v/v 1:1 methanol and acetonitrile) reduces the base line fluctuation and counteracts the decrease in EOF mobility for the presence of methanol.

The correlation between electrophoretic mobility of hydrophobic OPPs and the buffer concentrations was the result of the direct influence of EOF mobility. A linear decrease of EOF with an increase of buffer concentration was explained through the change of electrical double layer potential of the capillary wall and with respect to the increase of viscosity of the electrophoretic medium. The covariance statistics showed that differential influences on the linear decrease of EOF mobility with respect to phosphate and mixed buffer concentration were significantly different and the reason could be the presence of borate part in the mixed buffer. Addition of methanol or mixed modifier also clearly demonstrates their specific influences on the migration, and therefore, EOF was found to be significantly different. Covariance statistics also showed that their differential influences on the linear decrease of EOF mobility were significantly different, for which presence of acetonitrile was thought to be the reason. Most importantly, if the sample was prepared in a similar buffer matrix to the separation buffer, sensitivity of each pesticide was found to increase significantly and the LODs reduced at least one order lower. In strong EOF condition (highly basic separation buffer), electrokinetic injection with certain potential (15 kV) was found complementary for the same injection time in hydrodynamic injection with a certain pressure levels of 2.8 kPa that implied the neutrality of hydrophobic OPPs in the matrix.

With the level of organic modifier (10 % 1:1 v/v methanol and acetonitrile), the capacity factor (k) values of each pesticide were found to be independent of buffer within the range of 5 – 10 mM, indicating that the variation in elution window was negligibly small due to the proportional decrease in EOF mobility. An approach was proposed to estimate the k values using the coefficient of regression lines based

on the curvilinear relationship between retention time and applied potentials, which can be considered as an alternative way to apprehend the k values of OPPs. Relationship between $\log k$ and $\log K_{ow}$ (log value of octanol/water partition coefficient of OPPs) was found linear with better fit when mean of all referred $\log K_{ow}$ values were used. It was assumed that when the direct measurement of $\log K_{ow}$ of a particular pesticide would be difficult, then estimation of $\log K_{ow}$ values using proposed simple linear model of predicting $\log k$ can justifiably be used if the test compounds possess similar chemical properties.

Chapter 5 is the adoptions of outcomes in Chapter 4 with few modifications in it to develop methods for practical purpose, where several MEKC methods were demonstrated for the separation of hydrophobic OPPs and were compared through the quantitative aspects. Therefore a number of calibration lines were constructed to calculate the LODs of hydrophobic OPPs and the possibility of common online concentration techniques was tried and the corresponding sensitivity improvement were shown. Separation with SDS surfactant in basic buffer and positive applied potential (NM-MEKC-SDS) was found promising in terms of baseline separation and adoption of online concentration procedure. However, separation in acidic buffer with SDS surfactant and negative potential (RM-MEKC-SDS) was found to be limited as the short optimization scheme could not resolve the co-elution of few OPPs. Considering the selective effect in MEKC and for better resolution and/or higher sensitivity, β and γ -CD was added in NM-MEKC-SDS, but was found unproductive in either case. The role of a different surfactant, sodium cholate, (SC) was investigated in relation with micellar features, therefore, method was also developed using a pre-optimized level of SC with same level of buffer and modifier that was used in NM-MEKC-SDS, to compare the overall separation aspects in both surfactant systems. However, both surfactants were found to be quite comparable in terms of LODs and total analysis time but the use of SC surfactant resulted in a better separation of OPPs with higher efficiency and better resolution especially between profenofos and chlorpyrifos peaks. Therefore it was assumed that use of SC in MEKC separation for the hydrophobic OPPs, or generally any hydrophobic compounds could be a good selection.

Sensitivity enhancement factors (SEF, in terms of peak areas or peak heights) were found to be at least one order higher and LODs of sub-ppm ranges were attained for three hydrophobic OPPs (diazinon, quinalphos and profenofos) by the sweeping phenomenon in NM-MEKC-SDS. The potential of the method was studied through spiking the detectable levels of OPPs in natural water samples.

In Chapter 6, MEKC based separation of hydrophilic OPPs (phosphamidon, dicrotophos, monocrotophos) was studied and the possibility of obtaining lower LODs by adopting suitable online concentration methods was examined. The final method offered LODs in sub-ppm range, that was obtained by stacking the sample in a large injection time and separation was done in highly acidic buffer (SRMM). Spiked levels (ca. 1 ppm) in a natural lake water sample were clearly detected and the calculated quantities were about 100 % recovery.

Both proposed methods, sweeping-NM-MEKC-SDS for three hydrophobic OPPs and SRMM for three hydrophilic OPPs were expected to be useful either by direct injecting the sample upon filtration or with prior suitable offline pre-concentration steps. If the contamination levels of those water soluble pesticides in natural water are in the same or higher order of those LODs, then the real water samples can be analyzed directly upon filtration for removing the colloidal portions and being prepared in the desired matrices. Otherwise, suitable offline pre concentration steps (e.g. solid phase extraction or liquid-liquid extraction) would be required to enrich the samples to be the detectable levels. Both methods demonstrated a good linearity in the calibration and RSD values for migration, peak height and peak areas were usually less than 5 %.

Finally in Chapter 7, a very concise conclusion is given as all three preceding chapters are contained elaborate conclusions on the findings. Illustration about the future wider scope of MEKC in separation analysis is also stated by indicating the current trend of researches that are attempted to overcome its major drawbacks in sensitive detection capability. In addition to that, limitations of these separations of hydrophobic and hydrophilic OPPs by the developed MEKC methods are addressed and possibility of further improvement in future studies is also recommended.

effect of changes in temperature on separation selectivity would be worth trying, but not considered here due to the limited capability of the instrument.

Microemulsion electrokinetic capillary chromatography (MEEKC), a further modification of MEKC is a relatively new separation technique that has not been widely applied to a range of applications. However, impressions are expressed that the selectivity in MEEKC can be readily manipulated using variety of operating parameters. The separation basis in MEEKC is similar to that involved in MEKC where an oil droplets are coated with a surfactant (SDS commonly used) to reduce the surface tension between the two liquid layers which allows the emulsion to form. Therefore, the situation allows partitioning of the solute between the oil and water phases in a chromatographic fashion. Hydrophobic solutes would reside more comfortably in the oil droplets and easy to penetrate the surface of the droplet than the surface of a micelle which is much more rigid. This ability allows MEEKC to be applied to a wider range of solutes, especially for these hydrophobic OPPs.

Therefore, an enormous amount of research work need to be done with respect to optimizing the whole system involved for the separation of more hydrophobic compounds, adoption of suitable online concentration methods, compatible to more sensitive detectors, for which MEKC is not currently a preferred methodology.

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