

DISPERSIVE LIQUID-LIQUID MICROEXTRACTION METHODS  
FOR THE DETERMINATION OF TRIAZINE HERBICIDES  
IN AQUEOUS SAMPLES

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DISPERSIVE LIQUID-LIQUID MICROEXTRACTION METHODS  
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IN AQUEOUS SAMPLES

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*In the name of Allah, the Most Merciful and the Most Beneficent*

*This thesis is dedicated to my parents and my husband*

*Abdelhamid Mansor who has supported me all the way since the*

*beginning of my studies.*

*To my brothers and my family members.*

*To all those who believe in the richness of learning.*

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## ABSTRACT

Dispersive liquid-liquid microextraction (DLLME) and dispersive liquid-liquid microextraction based on solidification of floating organic droplets (DLLME-SFO) methods coupled with gas chromatography-mass spectrometry (GC-MS) were developed for the determination of triazine herbicides in aqueous samples. Four triazine herbicides were investigated, namely simazine, atrazine, secbumeton and cyanazine. In the optimized DLLME method, a mixture of chlorobenzene (20  $\mu$ L) as extraction solvent and 1 mL of acetone as disperser solvent was rapidly injected into the sample solution containing 4% (w/v) of NaCl. After 6 min centrifugation at 4000 rpm at room temperature, the fine chlorobenzene droplets settled at the bottom of the conical test tube. The settled phase (2  $\mu$ L) was injected into a gas chromatograph for analysis. The DLLME method gave good limits of detection (LOD) for the selected triazine herbicides ranging from 0.1 to 0.8  $\mu$ g/L and showed good linearity ranging from 0.1-1000  $\mu$ g/L with coefficient of estimation ( $r^2$ ) of 0.999. Good enrichment factors were obtained in the range of 145-188 for most of the analytes. In the optimized DLLME-SFO method, 1-undecanol (10  $\mu$ L) was mixed with 100  $\mu$ L of acetonitrile as disperser solvent and the mixture was then injected into sample solution containing 5% (w/v) NaCl. After the formation of cloudy state and centrifugation for 3 min at 4000 rpm at room temperature, the mixture was separated into two phases where the fine droplets of 1-undecanol floated to the top. The test tube was then placed in ice bath for cooling and solidification. The solidified extractant was transferred into small vial where it melted and was then injected into GC-MS for analysis. The DLLME-SFO method gave low LOD ranging from 0.008-0.037  $\mu$ g/L, high enrichment factors of 195-322 and good repeatability with RSD<5.1 %. The method also showed good linearity over the concentration range of 0.01-100  $\mu$ g/L for all target triazines. Both methods were applied for the analysis of selected water samples and sugarcane samples. The relative recoveries of DLLME and DLLME-SFO were excellent, ranging from 96.3-130.7% and 95.7-116.9%, respectively. The results showed that the DLLME-SFO method was more efficient and sensitive than the DLLME method.

## ABSTRAK

Pengekstrakan mikro cecair-cecair serakan (DLLME) dan pengekstrakan mikro cecair-cecair serakan berdasarkan pemejatan organik terampai (DLLME-SFO) berganding dengan kromatografi gas-spektrometri jisim (GC-MS) telah dibangunkan bagi penentuan racun rumpai triazin di dalam sampel akueus. Empat racun rumpai triazin telah dikaji iaitu simazin, atrazin, sekbumeton dan sianazin. Dalam kaedah DLLME yang telah dioptimumkan, campuran klorobenzena (20  $\mu\text{L}$ ) sebagai pelarut pengekstrak dan 1 mL aseton sebagai pelarut penyebar disuntik segera ke dalam larutan sampel yang mengandungi 4% (w/v) NaCl. Selepas pengemparan selama 6 minit pada 4000 rpm pada suhu bilik, butiran halus pelarut klorobenzena terenap di dasar tabung uji. Fasa terenap (2  $\mu\text{L}$ ) disuntik ke dalam alat kromatografi gas bagi dianalisis. Kaedah DLLME ini memberikan had pengesanan (LOD) rendah antara 0.1 hingga 0.8  $\mu\text{g/L}$  bagi analisis racun rumpai triazin dan menunjukkan kelinearan baik dalam julat 0.1-1000  $\mu\text{g/L}$  dengan pekali penentuan ( $r^2$ ) 0.999. Faktor pengkayaan yang baik telah diperolehi dalam julat 145-188 bagi kebanyakan analit. Dalam kaedah DLLME-SFO yang optimum, 1-undekanol (10  $\mu\text{L}$ ) dicampur dengan 100  $\mu\text{L}$  asetonitril sebagai larutan serakan dan campuran itu disuntik ke dalam larutan sampel yang mengandungi 5% (w/v) NaCl. Setelah larutan keruh terjadi dan pengemparan selama 3 minit pada 4000 rpm pada suhu bilik, campuran terpisah menjadi dua fasa di mana butiran halus 1-undekanol terapung di bahagian atas. Tabung uji itu diletakkan di dalam rendaman ais bagi penyejukan dan pemejatan. Ekstrak yang membeku dipindahkan ke dalam vial di mana ia menjadi cecair dan kemudian disuntik ke dalam GC-MS bagi analisis. Kaedah DLLME-SFO ini memberi LOD rendah dalam julat 0.008-0.037  $\mu\text{g/L}$ , faktor pengkayaan tinggi iaitu 195-322 dan kebolehulangan yang baik dengan RSD<5.1%. Kaedah ini juga menunjukkan kelinearan baik pada julat kepekatan 0.01-100  $\mu\text{g/L}$  bagi semua triazin yang dikaji. Kedua-dua kaedah telah diaplikasi bagi analisis sampel air terpilih dan sampel tebu. Perolehan semula relatif bagi kedua-dua DLLME dan DLLME-SFO adalah sangat baik, iaitu dalam julat 96.3-130.7% dan 95.7-116.9%, masing-masing. Hasil kajian menunjukkan bahawa pada umumnya kaedah DLLME-SFO adalah lebih cekap dan peka berbanding kaedah DLLME.

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## LIST OF ABBREVIATIONS

BTEX	- Benzene, toluene, ethylbenzene and xylenes.
CAR	- Carboxen
CE	- Capillary electrophoresis
CO <sub>2</sub>	- Carbon dioxide
CPE	- Cloud-point extraction
CW	- Carbowax
DAD	- Diode-array detector
DI-SPME	- Direct immersion-solid phase microextraction
DLLME	- Dispersive liquid-liquid microextraction
DLLME-LSC	- Dispersive liquid-liquid microextraction with little solvent consumption
DLLME-SFO	- Dispersive liquid-liquid microextraction based on solidification of floating organic droplet
DLPME	- Dynamic liquid phase microextraction
DVB	- Divinylbenzene
ECD	- Electron capture detector
EF	- Enrichment factor
ER	- Extraction recovery
ETAAS	- Electrothermal atomic absorption spectrometry
FAAS	- Flame atomic absorption spectrometry
FID	- Flame ionization detector
FPD	- Flame photometric detector
GC	- Gas chromatography



GFAAS	-	Graphite furnace atomic absorption spectrometry
GLC	-	Gas-liquid chromatography
GSC	-	Gas-solid chromatography
HF-LPME	-	Hollow fiber-liquid phase microextraction
HLLE	-	Homogeneous liquid-liquid extraction
HOCs	-	Halogenated organic compounds
HPLC	-	High-performance liquid chromatography
HS-LPME	-	Headspace liquid phase microextraction
HS-SDME	-	Headspace-single drop microextraction
HS-SPME	-	Headspace solid phase microextraction
ICP-OES	-	Inductively coupled plasma-atomic emission spectroscopy
IL-DLLME	-	Ionic liquid based on dispersive liquid-liquid microextraction
ILs	-	Ionic liquids
LC	-	Liquid chromatography
LLC	-	Liquid-liquid chromatography
LLE	-	Liquid-liquid extraction
LME	-	Liquid microextraction
LOD	-	Limit of detection
LOQ	-	Limit of quantification
LPME	-	Liquid phase microextraction
LSC	-	Liquid-solid chromatography
LT-DLLME	-	Low toxic-dispersive liquid-liquid microextraction
MAE	-	Microwave-assisted extraction
MIP	-	Molecularly imprinted polymer
MS	-	Mass spectrometry
MS/MS	-	Tandem mass spectrometry
MSD	-	Mass spectrometry detector
NaCl	-	Sodium chloride
OCPs	-	Organochlorine pesticides
OPPs	-	Organophosphorus pesticides
OSPs	-	Organosulfur pesticides

PA	-	Polyacrylate
PAHs	-	Polycyclic aromatic hydrocarbons
PCBs	-	Polychlorinated biphenyl
PDLLME	-	Partitioned dispersive liquid-liquid microextraction
PDMS	-	Polydimethylsiloxane
RR	-	Relative recovery
RSD	-	Relative standard deviation
SBSE	-	Stir-bar sorptive extraction
SDME	-	Single drop microextraction
SFE	-	Supercritical fluid extraction
SIM	-	Selective ion monitoring
SME	-	Solvent microextraction
SPE	-	Solid phase extraction
SPME	-	Solid phase microextraction
TCD	-	Thermal conductivity detector
TCS	-	Triclosan
TPR	-	Template resins
UV	-	Ultraviolet detector
VWD	-	Variable wavelength detector

## LIST OF SYMBOLS

$C_{\text{added}}$	-	The concentration of known amount of standard which was spiked to the real sample
$C_{\text{found}}$	-	The concentration of analyte after addition of a known amount of standard in the real sample
$C_0$	-	The analyte concentration in the settled phase
$C_{\text{real}}$	-	The concentration of analyte in the real sample
$C_{\text{set}}$	-	Initial concentration of analyte
$V_{\text{aq}}$	-	Volume of the sample solution
$V_{\text{set}}$	-	Volume of the settled phase
$^{\circ}\text{C}$	-	Degree Celsius
$\mu\text{g}$	-	Micro gram
$\mu\text{L}$	-	Micro liter
$\mu\text{m}$	-	Micro meter
$\text{g}$	-	Gram
i.d.	-	Inner diameter
$\text{L}$	-	Liter
$\text{m}$	-	Meter
$\text{m/z}$	-	Mass-to-charge ratio
$\text{min}$	-	Minute
$\text{mL}$	-	Milliliter
$\text{mm}$	-	Millimeter
$\text{M}\Omega$	-	Megohm
$n_0$	-	Total analyte in aqueous phase
$n_{\text{set}}$	-	Total analyte extracted into the settled phase

$r^2$	-	Coefficient of estimation
rpm	-	Revolutions per minute
w/v	-	Mass/volume (mass concentration)

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## CHAPTER 1

### INTRODUCTION

#### 1.1 Background of Study

Triazine herbicides are recognized as herbicides which have been broadly used in agriculture over the recent decades. They are very important to obtain productions with high-yield, sustainable agriculture. They are also considered omnipresent environmental pollutants and by various mechanisms they can break through surface and ground water. Toxicity of triazine herbicides range from high toxicity to low toxicity. Additionally, from high exposures to triazines there is anxiety from possible carcinogenicity as well as other health problems which have long-term affect for example Parkinson's diseases (Costello *et al.*, 2009). The range of dangerous health problems that can be caused by triazine herbicides is ranging from skin rashes to death. Moreover, small amounts of these compounds in environmental cause large effects on the animals and humans, furthermore, they cannot be directly detected in the samples. Thus, sensitive analytical method is required for determining the low concentrations of triazine herbicides in environment samples.

Several traditional sample preparation methods, such as liquid-liquid extraction (LLE) and solid phase extraction (SPE) have been used for analysis of various compounds. However, these techniques have several drawbacks, for example LLE needs long-time procedures, limited enrichment factors, labor-intensive and complicated multi-stage operation. Furthermore, LLE requires relatively large amount of solvent which causes environmental pollution, and expensive for waste

treatment. SPE came to address the limitations in the LLE. SPE method reduces the total organic solvent consumption; analysis time and is cost effective by using cartridges or disc and plates, but it is still a multi-stage operation and complicated method.

Several new sample preparation methods have been developed such as solid phase microextraction (SPME) method to overcome these problems in LLE and SPE. SPME is simple, rapid, feasible and solvent-free method which has been developed by Arthur and Pawliszyn (1990). The extraction and pre-concentration of analytes in SPME can be simultaneously achieved from various types of samples. The analytes can be extracted by either directly immersing the solid phase in aqueous solutions, known as direct immersion (DI-SPME) or by immersing vapor phase above aqueous solution, known as headspace (HS-SPME). The target analytes are then transferred into the stationary phase, which is covered on to the fiber, from the aqueous phase or vapor phase.

SPME technique has been applied in many analytical fields such as pharmaceutical analysis (Snow, 2000; Legrand *et al.*, 2003; Fu *et al.*, 2005), food analysis (Mitani *et al.*, 2003) and environmental pollutant analysis (Arthur *et al.*, 1992; Su and Huang, 1999; Wan Ibrahim *et al.*, 2010a). Moreover, there are number of publications in environmental pollutant analysis for example, extraction of triazine herbicides (Perreau and Einhorn, 2006) in various environmental samples. However, SPME fiber is very expensive and fragile, since each fiber costs between 85 and 170 USD (Kokosa *et al.*, 2009), has a short lifetime and the problem of sample carry-over is possible and cannot be eliminated.

Liquid phase microextraction (LPME) have been established (Jeannot and Cantwell, 1996) to address some of these problem. LPME is simple, rapid, effective and low-cost sample preparation methods, which minimize the toxic organic solvents that are used to extract target analytes from environmental samples by using very small volume of solvent (microliter). Up to now, many variations of LPME have been developed to obtain sensitive and accurate methods for analysis such as single drop microextraction (SDME) (Jeannot and Cantwell, 1997; Ahmadi *et al.*, 2006)

hollow fiber–liquid phase microextraction (HF-LPME) (Zhang *et al.*, 2006), headspace liquid phase microextraction (HS-LPME) (Shen and Lee, 2003b) and dynamic liquid phase microextraction (DLPME) (He and Lee, 1997).

Recently, Rezaee *et al.* (2006) have developed dispersive liquid-liquid microextraction method (DLLME) as a novel and new liquid phase microextraction method. This new method is based on ternary component system. It is simple, rapid, gives high enrichment factor and high recovery. On the other hand the usage of extraction solvent such as chlorobenzene, carbon tetrachloride, tetrachloroethylene, which have higher density than water, toxic and environmentally unfriendly are the main weaknesses of DLLME method. In order to address some of these weaknesses, a new LME mode namely dispersive liquid-liquid microextraction based on solidification of floating organic droplet (DLLME-SFO) has been developed. Numerous works have been reported the applications of DLLME-SFO for the analysis of organic pollutants in various environmental samples such as halogenated organic compounds (HOCs), organochlorine pesticides and polycyclic aromatic hydrocarbons (PAHs) (Leong and Huang, 2008; Leong and Huang, 2009; Xu *et al.*, 2009). DLLME-SFO has been found to be simple, rapid and very sensitive method of analysis for hazardous compounds like triazine herbicides.

## **1.2 Problem Statement**

Contamination of water resources by triazine herbicides is one of the most damaging and widespread environmental effects of agricultural production. They are very mobile in the soil and with heavy rains they can be washed into nearby water bodies. Therefore, agricultural chemicals such as pesticides, fungicides, herbicides as well as their metabolites, which are considered hazardous compounds for the environmental and humans health, have a role in the contamination of water resources.



Generally, triazine herbicides (atrazine, simazine, cyanazine, secbumeton, and others) are a set of related compounds that can be used to some degree interchangeably and have similar adverse health effects. Significant risks of cancer may be posed to people who are exposed to high levels of triazines through residues in food and water and to workers who apply them directly. Cardiovascular damage and retinal and muscular degeneration can also be caused from chronic high exposure of triazine herbicides (Thayer and Houlihan, 2004.). Furthermore, high triazine herbicides exposure may cause heart and limb birth defects. Besides they are considered endocrine disruptors which imitate human hormones affecting the development of fetuses and small children. Thus, the necessity for developing sample preparation, extraction, pre-concentration and separation methods for the determination of triazine herbicides in real samples become very important to obtain sensitive and feasible method able to determine the lowest concentration levels of these compounds in environmental samples.

DLLME-SFO offers several advantages of sample preparation and extraction methods compared to DLLME method. Only few researches have introduced the use of DLLME-SFO method for the analysis of various organic compounds (Dai *et al.*, 2010). To the best of our knowledge, the use of DLLME-SFO for the analysis of triazine herbicides in aqueous samples has not been reported. In the present work, DLLME and DLLME-SFO combined with GC-MS are investigated and compared for the determination of selected triazine herbicides in aqueous samples.

### **1.3 Objectives of the Research**

The objectives of the research are

- i. To develop liquid phase microextraction methods termed dispersive liquid-liquid microextraction (DLLME) and dispersive liquid-liquid microextraction based on solidification of floating organic droplet (DLLME-SFO) for the determination of triazine herbicides from aqueous samples.

- ii. To optimize DLLME and DLLME-SFO parameters including type and volume of extraction solvent, type and volume of dispersive solvent, extraction time and effect of salt addition.
- iii. To apply the developed methods coupled with GC-MS detection to the analysis of triazine herbicides in selected water and sugarcane samples.
- iv. To compare between DLLME and DLLME-SFO method for the determination of triazine herbicides.

#### **1.4 Significance of the Research**

This research introduces two simple, rapid and sensitive microextraction methods namely dispersive liquid-liquid microextraction (DLLME) and dispersive liquid-liquid microextraction based on solidification of floating organic droplet (DLLME-SFO) coupled with GC-MS for the determination of triazine herbicides in aqueous samples. In DLLME-SFO method, low-toxicity organic solvent which has lower density than water was used. Furthermore, the extractant droplet can be collected easily by solidifying it at low temperature. Thus, this method contributes towards green chemistry and maintains the environmental water resources and humans health from hazardous compounds.

#### **1.5 Scope of the Research**

In the present work, the two proposed methods namely DLLME and DLLME-SFO combined with GC-MS were developed for the determination of four selected triazine herbicides namely atrazine, simazine, cyanazine and secbumeton in aqueous samples. The effects of different experimental parameters, such as kind of extraction and disperser solvents, volume of extraction and disperser solvents, extraction time and effect of salt addition were studied for both DLLME and

DLLME-SFO methods. The performances of the two methods for the analysis of aqueous samples were tested and compared.

## **1.6 Outline of the Thesis**

This thesis consists of five chapters. Chapter 1 presents background of study, problem statement, research objectives, significance and scope of the research. Chapter 2 compiles the literature review, uses and effects of compounds studied, development of sample preparation methods in analytical chemistry as well as some applications in each type and chromatographic and separation techniques combined with DLLME and DLLME-SFO methods. Chapter 3 describes the extraction of selected triazine herbicides using conventional DLLME from various aqueous samples as well as the separation of these triazenes by using GC-MS technique. Several important extraction parameters such as type and volume of extraction solvent, type and volume of disperser solvent, extraction time and effect of salt addition were optimized. Chapter 4 displays experiments and results of DLLME-SFO method coupled with GC-MS for the determination of triazine herbicides in aqueous samples and the comparison between conventional DLLME and DLLME-SFO methods Chapter 5 summarizes this thesis by presenting the overall conclusions and suggestions for future research.

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