LIQUID AND SOLID PHASE MICROEXTRACTION METHODS FOR THE ANALYSIS OF ORGANIC ENVIRONMENTAL POLLUTANTS

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ABSTRACT

This work involves the investigation of new approaches and applications in miniaturized sample preparation techniques based on liquid phase and solid phase microextractions. A two-phase hollow fiber liquid phase microextraction (HF-LPME) method combined with gas chromatography-mass spectrometry was developed for the determination of selected polycyclic aromatic hydrocarbons (PAHs) in fresh milk. Under optimized conditions, low detection limits (LODs) were obtained ranging from 0.07-1.4 µg L^{-1} with relative recoveries of 85-110% which were higher than those obtained by conventional solvent extraction for the volatile PAHs. Agarose film liquid phase microextraction (AF-LPME) was developed for the extraction and preconcentration of PAHs in environmental water samples. Agarose, a green polymer, has been manipulated for different microextraction approaches. Agarose film was used as an interface between donor and acceptor phases which allowed for selective extraction of the analytes under optimum conditions. Under the optimum extraction conditions, the method showed good linearity in the range of 0.1–200 µg L^{-1}, low limits of detection (0.01-0.04 µg L^{-1}) and satisfactory relative recoveries (92.9-104.7%). AF-LPME device proved to be low-cost and thus reuse or recycle of the film was not required to eliminate the analytes carry-over between runs. A new microextraction technique termed agarose gel liquid phase microextraction (AG-LPME) was developed for the extraction of PAHs in water. Solvent-impregnated agarose gel disc used in AG-LPME was prepared by slicing gelled agarose and exchanging the solvent from water to ethanol and then to 1-octanol that functioned as the extractant and impregnation solvent. The solvent impregnated AG-LPME was found to be comparable with HF-LPME in terms of extraction efficiencies without solvent dissolution problems observed. The method offered high enrichment factors in the range of 89-177 and trace level LODs in the range of 9-14 ng L^{-1}. This technique combines extraction and preconcentration approaches using an environmentally-compatible solvent holder that fulfils the green chemistry concept. Due to the hydrophilic property of agarose, the selectivity of AG-LPME was evaluated on hydrophilic triazine herbicides. The AG-LPME showed significantly higher extraction efficiencies as compared to HF-LPME. The method offered superior enrichment factors in the range of 115-300 and trace LODs in the range of 0.02-0.04 µg L^{-1}. Multi-walled carbon nanotube-impregnated agarose film microextraction (MWCNT-AFME) combined with micro high performance liquid chromatography–ultraviolet detection has also been developed. The method utilized MWCNTs immobilized in agarose film which served as the adsorbent holder. The technique achieved trace LODs in the range of 0.1-50 ng L^{-1} for selected PAHs. The new MWCNT-AFME method was successfully applied to the analysis of spiked green tea beverage samples with good relative recoveries. The results supported the feasibility of agarose to serve as adsorbent holder in solid phase microextraction, thus saving the cost of chemical and waste disposal.

ABSTRAK

Kerja ini melibatkan kajian pendekatan dan aplikasi baru dalam teknik mini penyediaan sampel berdasarkan pengekstrakan mikro fasa cecair dan pepejal. Kaedah pengekstrakan mikro fasa cecair membran gentian berongga (HF-LPME) jenis dua fasa digabung dengan kromatografi gas-spektrometri jisim dibangunkan untuk menentukan hidrokarbon aromatik polisiklik (PAHs) dalam susu segar. Pada keadaan optimum, had pengesanan (LOD) rendah (0.07-1.4 µg L^{-1}) diperoleh dengan perolehan balik relatif 85-110% yang lebih tinggi daripada pengekstrakan pelarut konvensional untuk PAHs meruap. Pengekstrakan mikro fasa cecair filem agarosa (AF-LPME) dibangunkan untuk mengekstrak dan pra-memekatkan PAHs dalam air persekitaran. Agarosa, sejenis polimer hijau, telah dimanipulasikan untuk pendekatan pengekstrakan mikro berlainan. Filem agarosa digunakan sebagai antaramuka di antara fasa penderma dan penerima untuk membolehkan pengekstrakan selektif analit pada keadaan optimum. Pada keadaan pengekstrakan optimum, kaedah ini menunjukkan kelinearan baik dalam julat 0.1-200 µg L^{-1}, LOD rendah (0.01-0.04 µg L^{-1}) dan perolehan balik relatif memuaskan (92.9-104.7%). Oleh kerana peralatan AF-LPME berkos rendah, penggunaan semula atau pengitaran semula filem agarosa tidak diperlukan bagi menghindari pencemaran analit antara larian. Satu teknik pengekstrakan mikro baru dinamakan pengekstrakan mikro fasa cecair gel agarosa (AG-LPME) dibangunkan bagi menentukan PAHs dalam air. Cakera gel agarosa terkandung pelarut yang diguna dalam AG-LPME disediakan dengan memotong agarosa yang telah membentuk gel dan menukar pelarut daripada air kepada 1-oktanol yang berfungsi sebagai pelarut pengekstrak dan impregnasi. Kaedah ini didapati setanding dengan HF-LPME dari segi keberkesanan pengekstrakan tanpa masalah kehilangan pelarut. Kaedah ini menawarkan faktor pengkayaan yang tinggi (89-177) dan LOD aras surih dalam julat 9-14 ng L^{-1}. Teknik ini menggabungkan pengekstrakan dan pra-pemekatan menggunakan pemegang pelarut yang serasi dengan persekitaran dan bersesuaian konsep kimia hijau. Disebabkan sifat agarosa yang hidrofilik, kepilihan AG-LPME seterusnya dinilai menggunakan racun rumpai triazina hidrofilik. AG-LPME menunjukkan keberkesanan pengekstrakan yang ketara lebih tinggi berbandingkan HF-LPME. Kaedah ini menawarkan faktor pengkayaan unggul (115-300) dan LOD aras surih dalam julat 0.02-0.04 µg L^{-1}. Pengekstrakan mikro karbon tiub-nano berbilang dinding yang terkandung dalam filem agarosa (MWCNT-AFME) digabung dengan kromatografi cecair prestasi tinggi mikro-pengesanan ultra lembayung telah dibangunkan. Kaedah ini menggunakan karbon tiub-nano berbilang dinding yang tidak bergerak dalam filem agarosa untuk berfungsi sebagai pemegang bahan penjerap. Teknik ini mencapai LOD aras surih dalam julat 0.1-50 ng L^{-1} bagi PAHs terpilih. Kaedah MWCNT-AFME baru ini telah berjaya diaplikasi dalam analisis minuman teh hijau yang dipakukan dengan perolehan semula relatif yang baik. Keputusan kajian ini menyokong kebolehan agarosa untuk berfungsi sebagai pemegang bahan penjerap pengekstrakan mikro fasa pepejal dan menjimatkan kos bahan kimia dan pelupusan sisa.

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LIST OF ABBREVIATIONS

ACE	-	Acetone
ACT	-	Acetonitrile
AF	-	Agarose film
AF-LPME	-	Agarose film liquid phase microextraction
AG	-	Agarose gel
AG-LPME	-	Agarose gel liquid phase microextraction
AOAC	-	Association of Analytical Communities
ATR	-	Atrazine
BaP	-	Benzo[a]pyrene
BET	-	Brunauer Emmett Teller
CYN	-	Cyanazine
DAD	-	Diode array detector
DCM	-	Dichloromethane
DLLME	-	Dispersive liquid-liquid microextraction
DNA	-	Deoxyribonucleic acid
EF	-	Enrichment factor
EME	-	Electromembrane extraction
EtOH	-	Ethanol
EU	-	European Union
FD	-	Fluorescence detector
FESEM	-	Field emission scanning electron microscope
FLA	-	Fluoranthene
FLU	-	Fluorene
GC	-	Gas chromatography
HF	-	Hollow fiber
HF-LPME	-	Hollow fiber liquid phase microextraction
HPLC	-	High performance liquid chromatography

HS	-	Headspace
I.D.	-	Internal diameter
IL	-	Ionic liquid
IPA	-	Isopropyl alcohol
LLE	-	Liquid-liquid extraction
LOD	-	Limit of detection
LOQ	-	Limit of quantification
LPME	-	Liquid phase microextraction
LVI	-	Large volume injection
MASE	-	Membrane assisted solvent extraction
ME	-	Microextraction
MEPS	-	Microextraction in packed syringe
MRL	-	Maximum residue level
MS	-	Mass spectrometry
MWCNT-AF		Multi-walled carbon nanotube-impregnated agarose film
MWCNT-AFME	-	Multi-walled carbon nanotube-impregnated agarose film microextraction
MWCNTs	-	Multi-walled carbon nanotubes
NaCl	-	Sodium chloride
PAHs	-	Polycyclic aromatic hydrocarbons
PCBs	-	Polychlorinated biphenyls
PDA	-	Photodiode array
PDMS	-	Polydimethylsiloxane
PE	-	Polyethylene
PHE	-	Phenanthrene
PP	-	Polypropylene
PTV	-	Programmed temperature vaporization
PYR	-	Pyrene
RSD	-	Relative standard deviation
RTP	-	Room temperature phosphorimetry
SBSE	-	Stir bar sorptive extraction
SDME	-	Single drop microextraction
SE	-	Solvent extraction

SEC	-	Secbumeton
SFE	-	Subcritical fluid extraction
SFO	-	solidification of floating organic drop
SIM	-	Selected ion monitoring
SIR	-	Solvent impregnated resin
SPE	-	Solid phase extraction
SPME	-	Solid phase microextraction
SPMTE	-	Solid phase membrane tip extraction
SWE	-	Subcritical or superheated water extraction
THF	-	Tetrahydrofuran
USEPA	-	United States Environmental Protection Agency
UV	-	Ultraviolet
WHO	-	World Health Organization
μHPLC	-	Micro high performance liquid chromatography
μ-SPE	-	Micro solid phase extraction

LIST OF SYMBOLS

pK_a	-	Acid dissociation constant
n	-	Amount of analyte extracted by the coating
CO_2	-	Carbon dioxide
R^2	-	Coefficient of determination
C_W	-	Concentration of analyte in the aqueous sample solution
C_O	-	Concentration of analyte in the organic extraction solvent
r	-	Correlation coefficient
^oC	-	Degree Celsius
eV	-	Electronvolt
K	-	Equilibrium distribution coefficient
K_{fs}	-	Fiber coating/sample matrix distribution constant
V_f	-	Fiber coating volume
g	-	Gram
g mol^{-1}	-	Gram per mole
h	-	Hour
$C^0{}_w$	-	Initial amount of the analyte
C_0	-	Initial concentration of the analyte in the sample
kV	-	Kilovolts
L	-	Liter
m	-	Meter
µ	-	Micro
µg	-	Microgram
µg g^{-1}	-	Microgram per gram
µg kg^{-1}	-	Microgram per kilogram
µg L^{-1}	-	Microgram per liter
µm	-	Micrometer
mg	-	Milligram

$mg\ L^{-1}$	-	Milligram per liter
mL	-	Milliliter
mm	-	Millimeter
min	-	Minutes
ng	-	Nanogram
$ng\ L^{-1}$	-	Nanogram per liter
K_{ow}	-	1-octanol/water partitioning coefficients
ppb	-	Part per billion
%	-	Percent
p	-	Probability
rpm	-	Revolutions per minute
V_s	-	Sample volume
s	-	Seconds
V_w	-	Volume of aqueous sample solution
V_o	-	Volume of organic extraction solvent
w/v	-	Weight per volume

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CHAPTER 1

INTRODUCTION

1.1 Background of the Problem

Green Chemistry, a phrase first coined by the United States Environmental Protection Agency (USEPA) in the early 1990s as ‘to promote innovative chemical technologies that reduce or eliminate the use or generation of hazardous substances in the design, manufacture and use of chemical products’ (Environmental Protection Agency, 2008). Chemists are concerned about the future of the environment and are worried about what will happen if we continue to suffocate the earth with all the hazardous substance in chemical process. Therefore, it is important to design or develop greener chemical processes and to utilize sustainable development practices in order to eliminate environmental degradation and pollution.

Conventional extraction methods such as liquid-liquid extraction or solvent extraction based on organic solvents are generating hazardous wastes to the environment, and this has contradicted the concept of green chemistry which emphasises on chemical process or technology that improves the environment and quality of life (Sanghi and Srivastava, 2003).

In order to meet green chemistry requirements, eco-friendly extraction and innovations for a cleaner analysis is urged. Of this, solid phase microextraction (SPME) and liquid phase microextraction (LPME) have emerged as the latest green analysis to replace solid phase extraction (SPE) and liquid-liquid extraction (LLE).

The techniques are categorized as 'prevention' under the twelve principles of green chemistry proposed by Anastas and Warner in 1991 (Anastas and Warner, 2000).

1.2 Statement of Problem

Although the green techniques such as SPME and LPME have been increasingly developed and modified, the application of the techniques are still confined to the research institutes and universities. This is mainly because most of the green techniques were in-house validated. The food manufacturers and private industries' chemists are still employing the conventional technique such as LLE that was declared as standard reference method by some of the associations who established the maximum residue levels of food and environmental pollutants. Therefore, the publication of the green techniques should be made available to those associations and the public.

As fresh milk is used as one of the substitutes for breast milk during infancy, a rapid, selective, sensitive method is required to ensure the fresh milk is safe to be consumed. The monitoring of environmental pollutants residue levels is important to establish new maximum permitted levels. Existing method that uses conventional solvent extraction and fat saponification to extract environmental pollutants from milk consumes large amount of organic solvent and the procedures are tedious. Therefore, an environmentally green extraction method shall be developed to replace the existing solvent extraction method in order to reduce organic solvent usage and disposal costs. The liquid phase microextraction (LPME) promotes the reduction of hazardous substances in chemical processes for sample extraction and analysis.

In order to resolve the solvent dissolution problem that occurs during LPME, hollow fiber liquid phase microextraction (HF-LPME) has been developed to replace the core single drop microextraction (SDME). The extraction solvent or acceptor phase is well protected under impregnated hollow fiber made of polypropylene. However, solvent depletion problems are still frequently reported even though hollow fiber is used. In addition, although polypropylene is a recycled thermoplastic, the economic and environmental benefit of recycling is always an argument issue of the environmentalists. Therefore, an alternative material to protect acceptor phase in LPME is an urge to solve those problems.

1.3 Research Objectives

The objectives of this research are:

a. To develop and apply hollow fiber liquid microextraction (HF-LPME) method combined with gas chromatography–mass spectrometry (GC-MS) for the analysis of polycyclic aromatic hydrocarbons (PAHs) in fresh milk;
b. To develop an innovative LPME system using biodegradable material termed agarose film (AF) and solvent impregnated agarose gel (AG) LPME coupled with GC-MS for the analysis of PAHs in water samples;
c. To evaluate the selectivity of hydrophilic agarose towards hydrophilic triazine herbicides using solvent impregnated AG-LPME;
d. To develop an innovative multi-walled carbon nanotube-impregnated agarose film microextraction (MWCNT-AFME) combined with micro high performance liquid chromatography (μHPLC)-ultraviolet (UV) detection for the analysis of PAHs in green tea beverage samples.

1.4 Scope of the Study

Liquid phase microextraction techniques were thoroughly studied where the extraction performances of commercially available hollow fiber and innovations on biodegradable agarose were evaluated. Hollow fiber liquid phase microextraction (HF-LPME) technique was studied for the first time to extract lipophilic PAHs from fresh milk samples. Several important extraction parameters were optimized and sample pretreatment steps such as pH adjustment and ultrasonification of sample solutions have been omitted. Agarose which is generally used in biotechnology analysis as a medium of deoxyribonucleic acid (DNA) electrophoresis separation were prepared into film and solvent impregnated gel forms to serve as barriers or membranes of LPME to replace the hollow fiber. Several extraction parameters were explored and the newly developed technique was compared with LPME using commercially available HF for PAHs analysis as the reference method. The newly developed solvent--impregnated agarose gel LPME was thoroughly studied on its selectivity towards analytes which are more hydrophilic. Triazine herbicides were selected as model compounds. Several extraction parameters were comprehensively optimized and the optimum conditions were applied for the analysis of environmental and drinking water samples. The results were compared with those obtained by HF-LPME. An innovative agarose-immobilized sorbent film microextraction was studied, where multi-walled carbon nanotube (MWCNT)-impregnated agarose film was synthesized and applied as adsorbent film in solid phase microextraction (SPME). Several extraction parameters were thoroughly investigated and optimized for the analysis PAHs in green tea beverage samples.

1.5 Significance of Study

Modern life depends on the petrochemical and chemical related industries - most drugs, food, transportation, office equipments, paints, analysis and plastics are derived from oil and chemicals. It is difficult to imagine what will happen when petroleum-based starting materials become more expensive when the population growth is accelerated against world oil production. At the commencement of the new century, a shift in emphasis in green chemistry is apparent with the desire to develop more environmentally friendly routes. From a green chemistry viewpoint, the uses of green solvent and material have many advantages. The idea of ‘‘green’’ solvents or materials expresses the goal to minimize the environmental impact and reduce the waste produced and chemical related impact on human health resulting from the use of solvents in chemical process and analysis. For this reason, finding environmentally green-solvent and material have become a top priority of the chemists. Therefore, the use of less organic solvent and biodegradable material as extraction tools have formed the main thrust of a movement.

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