GAS CHROMATOGRAPHIC DETERMINATION OF STYRENE AND OTHER VOLATILE ORGANIC COMPOUNDS IN POLYSTYRENE FOOD PACKAGING

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Specially dedicated to my beloved husband, kids,

and family members

ACKNOWLEDGEMENTS

First and foremost I would like to thank God for His mercy and grace. His love and guidance has strengthened me through the good and tough times of my study.

I would like to thank my supervisor, Professor Dr. Mohd Marsin Sanagi, for his supervision, encouragement and thoughtful guidance throughout the project. I am indebted to his faith in me which motivated me to proceed and persist to complete my thesis.

I also wish to extend my sincere gratitude to my co-supervisors, Assoc. Prof. Dr. Wan Aini Wan Ibrahim and Assoc. Prof. Dr Ahmedy Abu Naim for their kindness and support. I would like to thank my post-graduate friends and all the members of the research group for their advice and support.

I would also like to thank the Ministry of Health and Public Service Department (JPA) for financial support and a studentship for myself. Many thanks should be given to the Public Health Laboratory of Johor Bahru (PHLJB) for providing laboratory facilities to make this research feasible. I am particularly grateful to the technical staffs of the Food Packaging Unit, PHLJB for their technical assistance.

I wish to extend a heartfelt appreciation to all of my family members who have given me encouragement and motivation, and have the utmost confidence in my endeavour. Last but not least, I must emphasize that I could not have persisted without my husband, Jimmy, for his love, support and understanding.

ABSTRACT

Testing of food packaging materials with reliable method gives consumers the assurance to the safety of the products. In this study, material and migration tests of styrene and other volatile organic compounds (VOCs) (toluene, ethylbenzene, iso-propylbenzene and *n*-propylbenzene) for polystyrene food packaging, using gas chromatography-flame ionization detection (GC-FID) are presented. In the material test, dissolution technique using dichloromethane was used to extract the analytes from the samples. The developed method was validated for specificity, detection limits, linearity, precision and accuracy. The applicability of the method to determine the targeted analytes in a number of commercial polystyrene food packaging was demonstrated. The results show that the dissolution technique with direct injection using GC-FID is effective for simultaneous analysis of five analytes in polystyrene food packaging. This direct injection method with limit of quantification (LOQ) of 8 mg/kg was lacking in sensitivity for migration study. Hence, headspace-solid phase microextraction (HS-SPME) technique was applied for migration test using water as food simulant. The effects of extraction variables including sample volume, elutropic strength, extraction temperature, extraction time, desorption time, sample agitation, and salt addition on the amounts of the extracted analytes were studied and optimal conditions were obtained for HS-SPME extraction. The method was validated, and the LOQ obtained at ppb and sub-ppb level was sensitive enough to detect the VOCs in the migration test. The optimized method was applied to test the analytes migration from polystyrene bowls and cups at storage temperatures ranging from 24°C to 80°C for 30 min. Styrene and ethylbenzene were observed to migrate from the samples into the food simulant. The migration of analyte was found to be strongly dependent upon the storage temperature. The maximum observed migration was from the polystyrene cup at simulating condition of 80°C for 30 min. The HS-SPME is useful as an alternative method to determine the migration of VOCs from food packaging material into food simulant.

ABSTRAK

Pengujian bahan pembungkus makanan dengan kaedah yang berkeyakinan boleh memberi jaminan kepada pengguna berkenaan keselamatan produk itu. Dalam kajian ini, ujian bahan dan ujian migrasi untuk stirena and sebatian mudah meruap (VOCs) yang lain (toluena, etilbenzena, iso-propilbenzena dan *n*-propilbenzena) bagi pembungkus polistirena dengan menggunakan kromatografi gas-pengesanan ion nyala (GC-FID) dibentangkan. Dalam ujian bahan, teknik pemelarutan menggunakan diklorometana telah digunakan untuk mengekstrak analit dari sampel. Keadah yang dibangunkan telah disahihkan bagi ketentuan, had pengesanan, lineariti, kejituan dan ketepatan. Penggunaan keadah tersebut bagi mengesan analit dalam beberapa jenis pembungkus makanan polistirena komersial telah diterangkan. Keputusan menunjukkan teknik pemelarutan dengan suntikan terus menggunakan GC-FID adalah berkesan untuk menganalisis lima jenis analit dengan serentak dalam pembungkus makanan polistirena. Kaedah suntikan terus mempunyai had kuantiti (LOQ) 8 mg/kg adalah kurang sensitif untuk ujian migrasi, jadi, teknik ruang kepala-pengekstrakan mikro fasa pepejal (HS-SPME) telah digunakan untuk ujian migrasi dan air digunakan sebagai makanan simulasi. Kesan pembolehubah pengekstrakan termasuk isipadu sampel, kekuatan elutropik, suhu pengekstrakan, masa pengekstrakan, masa nyahjerapan, pengacauan sampel, dan penambahan garam ke atas amaun analit terekstrak telah diuji dan keadaan optimum yang diperolehi telah digunakan untuk pengekstrakan HS-SPME. Kaedah ini telah disahihkan, dan LOQ yang didapati pada tahap ppb dan sub-ppb yang cukup sensitif untuk mengesan VOCs dalam ujian migrasi. Kaedah yang optimum telah digunakan untuk menganalisis analit yang berpindah dari mangkuk dan cawan polistirena pada suhu penyimpanan dengan julat dari 24°C ke 80°C. Stirena dan etilbenzena didapati telah berpindah dari sampel ke dalam makanan simulasi. Migrasi analit didapati bergantung kepada suhu penyimpanan. Migrasi yang maksimum telah didapati dari cawan polistirena pada keadaan simulasi 80°C selama 30 min. HS-SPME adalah berguna sebagai kaedah alternatif bagi penentuan migrasi VOCs dari pembungkus makanan ke dalam makanan simulasi.

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a	–	Intercept of regression line
ABS	–	Acrylonitrile butadiene styrene
ATR	–	Attenuated total reflection
b	–	Slope of regression line
BTEX	–	Benzene, toluene, ethylbenzene and xylene
C	–	Capacity
CE	–	Capillary electrophoresis
CFR	–	Code of Federal Regulations
CS_2	–	Carbon Disulphide
CW	–	Carbowax
CW-TPR	–	Carbowax – templated resin
DCM	–	Dichloromethane
DMA	–	Dimethylacetamide
DMF	–	Dimethylformamide
DNA	–	Deoxyribonucleic acid
DVB	–	Divinylbenzene
EB	–	Ethylbenzene
EC	–	European Commission
EPS	–	Expanded polystyrene
FDA	–	Food and Drug Administration
FT-IR	–	Fourier transform infrared spectroscopy
GC	–	Gas chromatography
GC-FID	–	Gas chromatography - flame ionization detection
GC-MS	–	Gas chromatography – mass spectrometry
GPPS	–	General purpose grade polystyrene
GRP	–	Glass reinforced plastic
HIPS	–	High impact grade polystyrene

HPLC	–	High performance liquid chromatography
HS-SPME	–	Headspace solid-phase microextraction
IARC	–	International Agency on Research for cancer
ICH	–	International Conference on Harmonization
I.D.	–	Internal diameter
IPB	–	iso-Propylbenzene
ISTD	–	Internal standard
IUPAC	–	International Union of Pure and Applied Chemistry
JHOSPA	–	Japan Hygienic Olefin and Styrene Plastics Association
KCl	–	Potassium chloride
LC-MS	–	Liquid chromatography - mass spectrometry
LLE	–	Liquid-liquid extraction
LOD	–	Limit of detection
LOQ	–	Limit of quantification
MAE	–	Microwave-assisted extraction
MEK	–	Methyl ethyl ketone
n	–	Number of samples or levels of standard solutions
NPB	–	*n*-Propylbenzene
OML	–	Overall migration limit
OLS	–	Ordinary least square regression
p	–	Number of replicates
PA	–	Polyacrylate
PAHs	–	Polycyclic aromatic compounds
PDMS	–	Polydimethylsiloxane
ppb	–	Part per billion
ppm	–	Part per million
ppt	–	Part per trillion
PS	–	Polystyrene
PTFE	–	Polytetrafluoroethylene
PVC	–	Polyvinyl chloride
QC	–	Quality control
r	–	Repeatability
RSD	–	Relative standard deviation
RT	–	Retention time

SA	–	Standard addition
SAN	–	Styrene acrylonitrile
S_b	–	Standard deviation of blank
S_{res}	–	Standard deviation of y-residuals
S_{y0}	–	Standard deviation of y-intercepts
SBR	–	Styrene butadiene rubber
SFE	–	Supercritical fluid extraction
SML	–	Specific migration limit
S/N	–	Signal-to-noise ratio
SPE	–	Solid-phase extraction
SPME	–	Solid-phase micorextraction
UV	–	Ultra violet
VOCs	–	Volatile organic compounds

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CHAPTER 1

INTRODUCTION

1.1 Food Packaging

Food packaging plays an important role to promote safe transportation, delivery and storage of food. Packaging makes food more convenient and gives the food greater safety assurance from microorganisms, biological and chemical changes such that the expensive and time consuming packaged foods can enjoy a longer shelf life [1]. In this modern society, packaging materials are also used for food preparation, and packaged foods are placed in ovens, microwaves, and even in boiling water. As a result, packaging becomes an indispensable element in the food sector.

With the advances in technology, various new packaging materials have been developed for food packaging applications. Plastic packaging technologies have been developing vigorously and some plastic containers have actually succeeded in replacing metal, glass and paper in many applications [2]. The main advantage in using plastics for packaging purposes is that most of the polymers have excellent physical properties such as strength and toughness, low weight and flexibility, as well as resistance to cracking [3].

The polymers used for plastic packaging materials are generally considered to be inert; however a large number of chemical adjuncts may be present in the finished products. These substances either added deliberately during manufacturing and processing or, unavoidably, as residues from polymerization reactions. The chemicals added include plasticizers, antioxidants, release compounds, heat and light stabilizers, lubricants, antistatic chemicals, adhesives, pigments, and many other compounds. The addition of such substances is essential to assist production processes or to enhance the properties and stability of the final product [3]. However, the use of such a wide range of chemicals inevitably gives rise to concern amongst both legislators and consumers. The problem was of particular concern since packaging can involve a long and intimate contact between the food and its container during storage at wholesale, retail outlets, and in the home.

1.2 Research Background

Among the major polymers used in food packaging, polystyrene (PS) has made up a large volume of the consumption of plastic containers. It is widely used as food service packaging because of its extremely strong yet lightweight, provides excellent insulation, and less expensive than many other food service packaging options. It is used for disposable cutlery, meat trays, yoghurt containers, clear eggs cartons, lids, vending cups and others. With the increasing popularity of convenience foods, polystyrene is most commonly used for packing of take-away foods in some fast-food joints, hawkers and food court outlets.

The usage conditions of polystyrene food packaging range from low temperatures for periods of days or weeks, for example packaged dairy and meat products, to high temperatures approaching the boiling point of water for short periods of time, for example vending cups and instant noodle bowls. The low molecular weight constituents present in the polystyrene plastic have the potential to migrate into the foodstuff in contact with the plastic especially during extended periods of time, or at the elevated temperatures. The principal classes of substances, which can migrate from polystyrene plastics to foods and beverages, are: residual monomers, low molecular weight components (oligomers) and various additives. Substances migrating to foodstuffs are of concern if they present a possible health hazard to the consumer, or cause unacceptable changes to the organoleptic properties of the food or beverages.

In Malaysia, food packaging is widely used due to the changing of food consumption patterns and increasing preferences for convenience and fast food. There is still lacking of controlling and monitoring of chemical residues in food packaging available in the market or food service establishment as well as regulatory compliance by packaging industries. Therefore, it is necessary to develop reliable and efficient method for testing of chemicals in food packaging materials in order to provide assurance to consumers about the safety of the product.

1.3 Statement of Hypothesis

The most tedious, labour intensive and important task encountered in the analytical laboratory is the sample preparation. Techniques to improve sample preparations are necessary in order to isolate the components of interest from the matrix prior to separation, identification and quantification. In the case of food packaging, the complexity and diversity of contaminants present in food packaging materials have resulted in the development of various analytical techniques for their extraction and analysis including microwave-assisted extraction (MAE), supercritical fluid extraction (SFE) and others. Numerous studies have focused on styrene monomer in polystyrene resins or specific foods and its migration to food or food simulants. However, only limited information is available on other volatile organic compounds (VOCs) in polystyrene food packaging and their migration. Based on the existing techniques available, it is expected that a simple, fast, reproducible and efficient analytical method could be developed for the determination of styrene and other volatile organic compounds simultaneously in polystyrene food packaging, and also their migration into food simulant.

1.4 Research Aim

The aim of this study is to develop a gas chromatographic method to determine residual styrene and other VOCs including toluene, ethylbenzene, iso-propylbenzene and *n*-propylbenzene in polystyrene food packaging and to study their migration into food simulant.

1.5 Research Objectives

The objectives of this research are as follows:

(i) To develop a simple extraction technique for residual styrene and other VOCs in polystyrene food packaging.

(ii) To apply solid-phase microextraction (SPME) technique to determine migration of styrene and other VOCs from polystyrene packaging into food simulant (water).

(iii) To study the performance characteristics of the developed method.

(iv) To apply the developed method for the determination of styrene and other VOCs in polystyrene food packaging samples and their migration into food simulant.

1.6 Scope of Study

The scope of research covers method development, method validation and applicability of method for sample testing. Analytes of interest were styrene and four other VOCs, namely toluene, ethylbenzene, iso-propylbenzene and *n*-propylbenzene. Method development includes material test and migration test of the analytes for polystyrene food packaging. In the case of material test, the analytes were extracted using dissolution method and detection using gas chromatography (GC). SPME with GC was used for migration study and water was chosen as food simulant. Experimental SPME conditions, which include sample volume, absorption and desorption time, temperature, stirring speed and ionic strength were optimized. Quantification of the analytes were achieved by internal standard calibration using 1,4-diethylbenzene as internal standard. The developed method was evaluated with different performance characteristics including limit of detection (LOD), limit of quantification (LOQ), linearity, precision and accuracy. The method was applied to the analysis of various kinds of commercially available polystyrene food packaging.

1.7 Outline of the Thesis

This thesis consists of six chapters. Chapter 1 introduces the research background, research aim, research objectives and scope of this study. Chapter 2 compiles the literature reviews including general information regarding styrene, its application in food packaging, and testing and legislation control of food packaging. Chapter 3 describes the experimental set up and the procedures applied in this study for testing of food packaging. Chapter 4 explains the development, validation and application of the method for determination of VOCs in polystyrene food packaging. Chapter 5 reports and discusses the results of SPME application to study the migration of VOCs from polystyrene food packaging into water as food simulant. The final chapter concludes the findings of this study and suggests areas for further research.