DEVELOPMENT OF METHOD FOR SIMULTANEOUS DETERMINATION OF PLASTICIZERS IN PLASTIC FOOD PACKAGING BY GAS CHROMATOGRAPHY

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DEVELOPMENT OF METHOD FOR SIMULTANEOUS DETERMINATION OF PLASTICIZERS IN PLASTIC FOOD PACKAGING BY GAS CHROMATOGRAPHY

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ABSTRACT

An analytical method has been developed for the simultaneous determination of plasticizers belonging to the classes of phthalates, adipates, sebacates, azelates, phosphates, glycolate, citrates, and trimellitates which are often present in plastic food packaging. Sample extraction consists of solvent dissolution, precipitation, centrifugation, and concentration steps before analysis by gas chromatography with flame ionization detector (GC-FID). The developed analytical procedure makes possible the simultaneous determination of 20 compounds in common plastic materials for food packaging industry, namely dimethyl phthalate, diethyl phthalate, diisopropyl phthalate, di-*n*-propyl phthalate, diisobutyl phthalate, di-*n*-butyl phthalate, dipentyl phthalate, di-*n*-butyl sebacate, acetyl-tri-*n*-butyl citrate, butylphthalyl butyl glycolate, butylbenzyl phthalate, dihexyl phthalate, di-2-ethylhexyl adipate, tri-2-ethylhexyl phosphate, dichlorohexyl phthalate, di-2-ethylhexyl phthalate, tri-*n*-butyl trimellitate, di-2-ethylhexyl azelate, di-*n*-octyl phthalate and tri-2-ethylhexyl trimellitate within 35 minutes of gas chromatographic separation. Performance characteristics of the method such as linearity range, detection and quantification limit, specificity, trueness and precision were studied and were found to be within the acceptable limit for each plasticizer type. With the limit of detection between 0.61 to 2.88 mg/kg, the method was successfully applied to the determination of plasticizers in plastic food packaging made of polyvinyl chloride, polyvinylidene chloride, polystyrene and polycarbonate. The method was found to be reliable, not labor intensive, suitable for general use and offer considerable time savings over the individual methods available to date. Thus, the proposed method could be used by many agencies including industries' own quality control laboratories and enforcement authorities in charge with ensuring plastic food packaging meet applicable regulations.

ABSTRAK

Suatu kaedah analisis telah dibangunkan untuk menganalisis secara serentak bahan pemplastik dari kumpulan ftalat, adipat, fosfat, trimellitat, azelat, sitrat dan sebakat yang biasa digunakan dalam pembuatan plastik pembungkus makanan. Pengekstrakan sampel terdiri dari proses pemelarutan menggunakan bahan pelarut, pemendakan, pengemparan dan pemekatan sebelum analisis dijalankan menggunakan kromatografi gas dengan pengesan pengionan nyala (GC-FID). Kaedah analisis yang dibangunkan ini membolehkan pengenalpastian secara serentak sebanyak 20 sebatian pemplastik bagi jenis plastik biasa yang digunakan dalam industri pembungkusan makanan iaitu dimetil ftalat, dietil ftalat, diisopropil ftalat, di-*n*-propil ftalat, diisobutil ftalat, di-*n*-butil ftalat, dipentil ftalat, di-*n*-butil sebakat, asetil-tri-*n*-butil sitrat, butiltalilbutil glikolat, butilbenzil ftalat, diheksil ftalat, di-2-etilheksil adipat, tri-2-ethilheksil fosfat, dikloroheksil ftalat, di-2-etilheksil ftalat, tri-*n*-butil trimellitat, di-2-etilheksil azelat, di-*n*-oktil ftalat, dan tri-2-etilheksil trimellitat dalam tempoh 35 minit pemisahan kromatografi. Ciri-ciri prestasi kaedah seperti julat linear, had pengesanan dan kuantifikasi, kespesifikan, kejituan, dan kepresisan telah dikaji dan didapati berada dalam julat yang boleh diterima bagi setiap jenis bahan pemplastik. Dengan had pengesanan di antara 0.61 hingga 2.88 mg/kg, kaedah ini telah berjaya digunapakai untuk penentuan bahan pemplastik di dalam bahan plastik pembungkus makanan yang dibuat dari polivinil klorida, polivinilidin klorida, polistirena dan polikarbonat. Kaedah ini didapati boleh dipercayai, memberi beban kerja yang sedikit, mudah untuk digunakan dan menjimatkan masa berbanding kaedah individu yang digunakan pada masa ini. Justeru, kaedah ini boleh digunapakai oleh pelbagai agensi termasuk makmal kawalan mutu industri dan pihak penguatkuasaan tertentu untuk memastikan bahan pembungkus makanan plastik menepati peraturan yang berkenaan.

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LIST OF ABBREVIATIONS

AOAC	-	Association Officials of Analytical Chemistry
ATBC	-	Acetyl-tri-n-butyl citrate
BBP	-	Benzylbutyl phthalate
BPBG	-	Butyl phthalyl butyl glycolate
CRM	-	Certified reference materials
CV	-	Coefficient of variation
DBA	-	Dibutyl adipate
DBS	-	Dibutyl sebacate
DCHP	-	Dicyclohexyl phthalate
DEHA	-	Di-2-ethylhexyl adipate
DEHA8	-	Di-2-ethylhexyl azelate
DEHP	-	Di-2-ethylhexyl phthalate
DEP	-	Diethyl phthalate
DHpP	-	Di-*n*-heptyl phthalate
DHxP	-	Di-*n*-hexyl phthalate
DiBP	-	Diisobutyl phthalate
DiDP	-	Diisodecyl phthalate
DiNP	-	Diisononyl phthalate
DiPP	-	Diisopropyl phthalate
DMP	-	Dimetyl phthalate

DnBP	-	Di-*n*-butyl phthalate
DnOP	-	Di-*n*-octyl phthalate
DnPP	-	Di-*n*-propyl phthalate
DOS	-	Di-2-ethylhexyl sebacate
DPeP	-	Di-*n*-pentyl phthalate
FID	-	Flame Ionization Detector
FT-IR	-	Fourier Transform Infrared Spectroscopy
GC	-	Gas Chromatography
HDPE	-	High density polyethylene
HPLC	-	High Performance Liquid Chromatography
ICH	-	International Conference of Harmonization of Technical Requirements for Registration of Pharmaceutical for Human Use
ISO	-	The International Organization for Standardization
IUPAC	-	International Union of Pure and Applied Chemistry
LLPE	-	Linear low polyethylene
LOD	-	Limit of detection
LOQ	-	Limit of quantification
MAFF	-	Ministry of Agriculture, Fisheries and Food United Kingdom
MS	-	Mass spectrometry
PC	-	Polycarbonate
PE	-	Polyethylene
PET	-	Polyethylene tetraphthalate
PP	-	Polypropylene
PS	-	Polystyrene
PVA	-	Polyvinyl acetate
PVC	-	Polyvinyl chloride
PVdC	-	Polyvinylidene chloride
SD	-	Standard deviation
TBTM	-	Tri-n-butyl trimellitate
TCP	-	Tricresyl phosphate
TDI	-	Tolerable dietary intake

TOP	-	Tri-(2-ethylhexyl) phosphate
TOTM	-	Tri-(2-ethylhexyl) trimellitate
TPhP	-	Triphenyl phosphate
TTDI	-	Total tolerable dietary intake
UV	-	Ultra Violet

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CHAPTER 1

INTRODUCTION

1.1 Research Background

Plasticizer is a plastic additive that is not bound chemically in the plastics and can consequently penetrate these materials, and migrate into food that comes into contact. The presence of phthalates, a common plasticizer in packaging materials and their migration into packaged foods have been confirmed by a number of researchers (Balafas *et al*., 1999; MAFF, 1996; Nerin *et al*., 1993; Peterson & Breindahl, 2000; Tsumura *et al*., 2001a & b). The amount of plasticizers in packaged food depends on many factors including the concentration of plasticizers in the packaging material or printing ink, the storage period, the storage temperature, the fat content in the food and the contact area (Balafas *et al*., 1999).

Several methods have been reported for the determination of phthalate ester plasticizers such as gas chromatography (Castillo *et al*., 1999; Marin *et al*., 1996; Yasuhara *et al*., 1997) and high performance liquid chromatography (Castillo & Barcelo *et al*., 2001; Jara *et al*., 2001; Kelly & Larroque, 1999). Different pre-concentration methods have been used on different matrices such as solvent extraction for solid samples including foods (Tsumura *et al*., 2001a; Summerfield & Cooper, 2001; Peterson & Breindahl, 2000), and food packaging materials (Balafas *et al*., 1999; Song *et al*., 2000; Aurela *et al*., 1999). Other common extraction methods were also developed such as solid-phase extraction (Jara *et al*., 2001; Davis *et al*., 1999; Jonsson & Born, 2002), and solid-phase microextraction (Cai *et al*.,

2003a; Penalver *et al*., 2000; Prokupkova *et al*., 2002). It was found that thus far, there are only limited numbers of proposed analytical method for the simultaneous determination of all synthetic plasticizers group in any possible media.

1.2 Statement of Hypothesis

Since some plasticizers could pose a risk to public health, there is a need to have an analytical method to identify and quantify residues of concern in polymeric materials intended for food packaging. This work develops a single in-house method that can be used for simultaneous determination of twenty types of synthetic plasticizers included phthalates, phosphates, trimellitates, citrates, adipates and sebacates used in plastic food packaging. It is expected that such method is feasible using gas chromatography with flame ionization detector (GC-FID) or mass spectrometry (GC-MS).

1.3 Research Aim

The aim of this study was to develop a method for determination of plasticizers in plastic food packaging using gas chromatography. The method would be evaluated by investigating several performance criteria including its application to real samples.

1.4 Research Objectives

i. To develop a method for simultaneous determination of twenty types of synthetic plasticizers such as phthalates, phosphates, trimellitates, citrates, adipates and sebacates in plastic food packaging.

ii. To validate performance criteria of the established method including limit of detection and limit of quantification, calibration and linear range, specificity/selectivity, trueness and precision.

1.5 Scope of Study

The twenty types of synthetic plasticizers as listed in Table 1.1 were studied. The table also presents their corresponding abbreviations, general name, Chemical Abstract Service Registration Number (CASRN) and molecular mass. The established method was validated to ensure that it fits the purpose before being used in routine laboratory works.

1.6 Outline of the Thesis

This thesis consists of six chapters. Chapter 1 presents general background of this study, research aim, research objectives and scope. Chapter 2 compiles the literature review and theoretical background on method validation protocols for determination of plasticizers in plastic food packaging. The procedures for assessing performance criteria of the established method are presented in Chapter 3. Chapter 4 reports the results and discusses the performance criteria for determination of plasticizers in plastic food packaging by gas chromatography coupled with flame ionisation detector and mass spectrometry for confirmation. It also elaborates the applicability of the method to determine plasticizers in commercial plastic food packaging made of polystyrene, polyinyl chloride, polyvinylidene chloride and polycarbonate. The concluding Chapter 5 summarizes this thesis by presenting the overall conclusions and suggestions for future study.

Table 1.1. List of 20 plasticizers studied

No.	Plasticizer name	Abbreviation	CASRN*	Molecular mass (g/mol)
1	Diethyl phthalate	DEP [a,b]	84-66-2	222.2
2	Di-iso-propyl phthalate	DiPP	605-45-8	250.3
3	Di-*n*-propyl phthalate	DnPP [a]	131-16-8	250.3
4	Di-iso-butyl phthalate	DiBP	84-69-5	278.3
5	Di-*n*-butyl sebacate	DBS	109-43-3	314.5
6	Butylphthalyl butylglycolate	BPBG	85-70-1	336.4
7	Dihexyl phthalate	DHxP [a]	84-75-3	334.4
8	Dicyclo hexyl phthalate	DCHP [a]	84-61-7	330.4
9	Tri-*n*-butyl trimellitate	TBTM	1726-23-4	378.5
10	Di-2-ethylhexyl azelate	DEHA8	103-24-2	412.6
11	Dimethyl phthalate	DMP	131-11-3	194.2
12	Di-*n*-butyl phthalate	DnBP [a,b,c]	84-74-2	278.3
13	Dipentyl phthalate	DPeP [a]	131-18-0	306.4
14	Acetyl-tri-*n*-butyl citrate	ATBC	77-90-7	402.5
15	Butylbenzyl phthalate	BBP [a,b,c]	85-68-7	312.4
16	Di-2-ethylhexyl adipate	DEHA [a]	103-23-1	370.6
17	Tri-2-ethylhexyl phosphate	TOP	78-42-2	434.6
18	Di-2-ethylhexyl phthalate	DEHP [a,b,c]	117-81-7	390.6
19	Di-*n*-octyl phthalate	DnOP	117-84-0	390.6
20	Tri-2-ethylhexyl trimellitate	TOTM	3319-31-1	546.8

Note:

[a] Suspected endocrine disruptor chemicals by Japan Environmental Agency (1998)
[b] Priority toxic pollutants by United States EPA (1999)
[c] Suspected endocrine disruptor chemicals by European Parliment (2001)
*CASRN (ACS, 2007)

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