

学校编码: 10384

分类号_____密级_____

学号: 20051301813

UDC _____

廈門大學

碩 士 学 位 论 文

食品和塑料橡胶中酞酸酯的 GC-EI/MS 及
GC-MS/MS 分析方法研究

Study of Phthalic Acid Esters in Food and Plastics rubber
by GC-EI/MS and CG-MS/MS

孙若男

指导教师姓名: 林竹光 副教授

专业名称: 分析化学

论文提交日期: 2008年5月

论文答辩时间: 2008年6月

学位授予日期: 2008年 月

答辩委员会主席: _____

评 阅 人: _____

2008年 月

Dissertation for Master of Analytical Chemistry

**Study of Phthalic Acid Esters in Food and Plastics rubber
by GC-EI/MS and CG-MS/MS**

**By
Ruonan Sun**

**Supervised by
Associate Professor Zhuguang Lin**

**College of Chemistry & Chemical Engineering
Xiamen University**

June, 2008

厦门大学学位论文原创性声明

兹提交的学位论文，是本人在导师指导下独立完成的研究成果。本人在论文写作中参考的其他个人或集体的研究成果，均在文中以明确方式标明。本人依法享有和承担由此论文产生的权利和责任。

声明人（签名）：

年 月 日

厦门大学学位论文著作权使用声明

本人完全了解厦门大学有关保留、使用学位论文的规定。厦门大学有权保留并向国家主管部门或其指定机构送交论文的纸质版和电子版，有权将学位论文用于非赢利目的的少量复制并允许论文进入学校图书馆被查阅，有权将学位论文的内容编入有关数据库进行检索，有权将学位论文的标题和摘要汇编出版。保密的学位论文在解密后适用本规定。

本学位论文属于

- 1、保密 ()，在 年解密后适用本授权书。
- 2、不保密 ()

(请在以上相应括号内打“√”)

作者签名:

日期: 年 月 日

导师签名:

日期: 年 月 日

摘要	i
ABSTRACT	iii
第 1 章 绪论	1
1.1 酞酸酯简介	1
1.1.1 PAEs 的理化性质	3
1.1.2 PAEs 的环境污染	4
1.1.2.1 大气污染	4
1.1.2.2 水污染	5
1.1.2.3 土壤和沉积物污染	6
1.1.2.4 生物体污染	8
1.1.3 PAEs 的危害	8
1.1.3.1 PAEs 对生态系统的影响	8
1.1.3.2 PAEs 对人体的影响	9
1.2 PAEs 的国内外研究现状	9
1.2.1 样品的前处理方法	9
1.2.1.1 液-液萃取法	10
1.2.1.2 固相萃取法	10
1.2.1.3 固相微萃取法	11
1.2.1.4 索氏提取法	12
1.2.1.5 超临界流体萃取法	12
1.2.1.6 超声提取法	13
1.2.1.7 微波辅助萃取法	13
1.2.2 分析检测方法	14
1.2.2.1 气相色谱法 (GC)	14
1.2.2.2 高效液相色谱法 (HPLC)	15
1.2.2.3 毛细管电色谱法	15
1.2.2.4 平面色谱法	15
1.3 课题意义及研究内容	16
1.4 课题展望	17
参考文献 1	

第 2 章 动物内脏中 14 种酞酸酯类环境激素残留的 GC-EI/MS 分析方法的建立	24
2.1 NIST 标准谱图及初步解析	25
2.1.1 DMP 的 EI/MS 标准谱图与初步解析	27
2.1.2 DMIP 的 EI/MS 标准谱图与初步解析	28
2.1.3 DEP 的 EI/MS 标准谱图与初步解析	29
2.1.4 DAP 的 EI/MS 标准谱图与初步解析	30
2.1.5 DPrP 的 EI/MS 标准谱图与初步解析	31
2.1.6 DIBP 的 EI/MS 标准谱图与初步解析	32
2.1.7 DBP 的 EI/MS 标准谱图与初步解析	33
2.1.8 DMEP 的 EI/MS 标准谱图与初步解析	34
2.1.9 DEEP 的 EI/MS 标准谱图与初步解析	35
2.1.10 DPP 的 EI/MS 标准谱图与初步解析	36
2.1.11 BBP 的 EI/MS 标准谱图与初步解析	37
2.1.12 DCHP 的 EI/MS 标准谱图与初步解析	38
2.1.13 DEHP 的 EI/MS 标准谱图与初步解析	39
2.1.14 DPhP 的 EI/MS 标准谱图与初步解析	40
2.1.15 DOP 的 EI/MS 标准谱图和初步解析	41
2.2 仪器与试剂	42
2.2.1 主要仪器	42
2.2.2 主要试剂	43
2.3 实验内容	44
2.3.1 动物内脏样品的前处理	44
2.3.2 GC-EI/MS 分析条件	44
2.4 结果与讨论	45
2.4.1 动物内脏样品前处理条件的优化与选择	45
2.4.2 GC-EI/MS 分析方法的优选	50
2.4.3 分析空白值的控制	52
2.4.4 线性方程、相关系数与方法检测限	53
2.4.5 加标回收率及相对标准偏差	54
2.4.6 动物内脏样品的分析	56
2.5 小结	57
参考文献 2	57

第 3 章 蔬菜中 16 种 PAEs 残留的 GC-MS 分析研究	57
3.1 仪器与试剂	58
3.1.1 主要仪器.....	58
3.1.2 主要试剂.....	58
3.2 实验内容	58
3.2.1 蔬菜样品的前处理.....	58
3.2.2 GC-EI/MS 分析条件.....	59
3.3 结果与讨论	60
3.3.1 蔬菜样品前处理条件的优化与选择.....	60
3.3.2 内标物 BB 和目标物 DPhIP 的 EI/MS 的谱图解析.....	62
3.3.3 GC-EI/MS SIM 分析.....	67
3.3.4 线性方程、相关系数与方法检测限.....	71
3.3.5 加标回收率及相对标准偏差.....	71
3.3.6 蔬菜样品的分析.....	71
3.4 小结	72
参考文献 3	73
第 4 章 塑料橡胶制品中 13 种 PAEs 的 GC-EI/MS 分析方法研究	73
4.1 仪器与试剂	74
4.1.1 主要仪器.....	74
4.1.2 主要试剂.....	74
4.2 实验内容	74
4.2.1 塑料橡胶制品的前处理.....	74
4.2.2 GC-EI/MS 分析条件.....	75
4.3 结果与讨论	77
4.3.1 塑料橡胶制品前处理条件的优化与选择.....	77
4.3.2 GC-EI/MS SIM 分析.....	78
4.3.3 线性方程、相关系数与方法检测限.....	79
4.3.4 加标回收率及相对标准偏差.....	80
4.3.5 塑料橡胶制品的分析.....	81
4.4 GC-EI/MS SIM 分析方法的评价[11]	83

4.4.1 方法检测限 (Limit of Detection, LOD)	83
4.4.2 准确度 (Accuracy)	83
4.4.3 精密度 (Precision)	83
4.4.4 线性范围 (Linear range)	84
4.5 小结	84
参考文献 4	85
第 5 章 8 种酞酸酯的气相色谱-离子阱串联质谱分析方法初探	87
5.1 EI-MS/MS 分析方法原理简介	88
5.1.1 EI-MS/MS 分析的基本原理	88
5.1.2 EI-MS/MS 分析的操作模式	88
5.1.3 EI-MS/MS 的特点	89
5.1.4 EI-MS/MS 技术的分类	89
5.1.5 串联质谱新技术的发展及应用进展	90
5.2 EI-MS/MS 分析方法的建立	91
5.2.1 仪器与试剂	92
5.2.2 色谱和质谱分析条件	92
5.2.3 EI-MS/MS 分析条件的选择	93
5.3 实验结果与讨论	99
5.3.1 PAEs 的 EI-MS/MS 谱图初步解析	99
5.3.2 线性回归方程、相关系数	101
5.3.3 EI-MS/MS 与离子存贮技术 (SIS) 的比较	104
5.4 小结	105
参考文献 5	106
结束语	107
在学期间发表和交流的论文	109
致谢	111
附录 1 中国环境优先控制污染物“黑名单”	113
附录 2 几种邻苯二甲酸酯类环境激素的用途和危害	114
附录 3 内标物和 17 种目标物的中英文名称、化学式、CAS 号及分子量	115
附录 4 17 种 PAEs 的简要理化性质	116

Abstract (Chinese)	i
Abstract (English)	iii
Chapter 1 Prolegomenon	1
1.1 The Brief Intoduction of Phthalic Acid Esters	1
1.1.1 Characters of PAEs..	3
1.1.2 The Environmental Pollution of PAEs.....	4
1.1.2.1 Air Pollution.....	4
1.1.2.2 Water Pollution.....	5
1.1.2.3 The Soil and Sediment Pollution.....	6
1.1.2.4 Organism Pollution.....	8
1.1.3 Harmfulness of PAEs.....	8
1.1.3.1 The Harmful toHolocoenotic.....	8
1.1.3.2 The Harmful to Human Body.....	9
1.2 Current Progress of PAEs Residue Analysis at Home and Abroad	9
1.2.1. Progress of Sample Pretreatment Technology.....	9
1.2.1.1 Liquid Liquid Extraction.....	10
1.2.1.2 Solid-Phase Extraction.....	10
1.2.1.3 Solid-Phase Microextraction.....	11
1.2.1.4 Soxhlet Extraction.....	12
1.2.1.5 Supercritical Fluid Extraction.....	12
1.2.1.6 Ultrasonic Extraction.....	13
1.2.1.7 Micro Amplitude Extraction.....	13
1.2.2 Progress of Multiresidue Determination of Pesticides.....	14
1.2.2.1 Gas Chromatography.....	14
1.2.2.2 Liquid Chromatography.....	15
1.2.2.3 Capillary Electrochromatography.....	15
1.2.2.4 Plane Chromatography.....	15
1.3 Meaning and Content of The Thesis	16
1.4 The Prospect of The Subject	17
Reference 1	17

Chapter 2 Development of A Method for Analyzing 14 Phthalic Acid

Esters Residue in Animal Innards by GC-MS	24
2.1 NIST Standard Spectrum With The Primary Parse	25
2.1.1 EI/MS Standard Spectrum of DMP With The Primary Parse.....	27
2.1.2 EI/MS Standard Spectrum of DMIP With The Primary Parse.....	28
2.1.3 EI/MS Standard Spectrum of DEP With The Primary Parse.....	29
2.1.4 EI/MS Standard Spectrum of DAP With The Primary Parse.....	30
2.1.5 EI/MS Standard Spectrum of DPrP With The Primary Parse.....	31
2.1.6 EI/MS Standard Spectrum of DIBP With The Primary Parse.....	32
2.1.7 EI/MS Standard Spectrum of DBP With The Primary Parse.....	33
2.1.8 EI/MS Standard Spectrum of DMEP With The Primary Parse.....	34
2.1.9 EI/MS Standard Spectrum of DEEP With The Primary Parse.....	35
2.1.10 EI/MS Standard Spectrum of DPP With The Primary Parse.....	36
2.1.11 EI/MS Standard Spectrum of BBP With The Primary Parse.....	37
2.1.12 EI/MS Standard Spectrum of DCHP With The Primary Parse.....	38
2.1.13 EI/MS Standard Spectrum of DEHP With The Primary Parse.....	39
2.1.14 EI/MS Standard Spectrum of DPhP With The Primary Parse.....	40
2.1.15 EI/MS Standard Spectrum of DOP With The Primary Parse.....	41
2.2 Instrument and Reagent	42
2.2.1 The Main Instrument.....	42
2.2.2 The Main Reagent.....	43
2.3 Experimental Part	44
2.3.1 The Pretreatment of The Animal Innards.....	44
2.3.2 The Conditions of GC-EI/MS.....	44
2.4 Result and Discussion	45
2.4.1 Optimization and Choice of Pretreatment Conditions.....	45
2.4.2 Optimization of GC-EI/MS Analytic Method.....	50
2.4.3 The Control of The Analytic Blank Value.....	52
2.4.4 Linear Equation, Correlation Coefficient and Method Detection Limit.....	53
2.4.5 Average Recovery and Relative Standard Deviation.....	54
2.4.6 Analysis of Animal Innards.....	56
2.5 Summary	57
Reference 2	57

Chapter 3 Multiresidue Determination of 16 PAEs in Vegetables by

GC-MS	57
3.1 Instrument and Reagent	58
3.1.1 The Main Instrument.....	58
3.1.2 The Main Reagent.....	58
3.2 Experimental Part	58
3.2.1 The Pretreatment of The Animal Innards.....	58
3.2.2 The Analytic Conditions of GC-EI/MS.....	59
3.3 Result and Discussion	60
3.3.1 Optimization and Choice of Pretreatment Conditions.....	60
3.3.2 .EI/MS Standard Spectrum of BB and DPhIP With The Primary Parse.....	62
3.3.3 GC-EI/MS Analytic Method.....	67
3.3.4 Linear Equation, Correlation Coefficient and Method Detection Limit.....	71
3.3.5 Average Recovery and Relative Standard Deviation.....	71
3.3.6 Analysis of Vegetables.....	71
3.4 Summary	72
Reference 3	73
Chapter 4 Analytical of 16 PAEs in Plastic Rrubber by GC-MS	73
4.1 Instrument and Reagent	74
4.1.1 The Main Instrument.....	74
4.1.2 The Main Reagent.....	74
4.2 Experimental Part	74
4.2.1 Optimization of Sample Pretreatment Technology.....	74
4.2.2 GC-EI/MS Analytic Method.....	75
4.3 Result and Discussion	77
4.3.1 Optimization and Choice of Pretreatment Conditions.....	77
4.3.2 GC-EI/MS Analytical Method.....	78
4.3.3 Linear Equation, Correlation Coefficient and Method Detection Limit.....	79
4.3.4 Average Recovery and Relative Standard Deviation.....	80
4.3.5 Analysis of Plastic Rubber.....	81
4.4 Method Performance for GC-EI/MS SIM	83

4.4.1	Limit of Detection(LOD)	83
4.4.2	Accuracy	83
4.4.3	Precision	83
4.4.4	Linear Range	84
4.5	Summary	84
Reference 4		85
Chapter 5 Establishment of GC-EI-MS/MS Analytical Method for 8		
	PAEs	87
5.1	Principle for EI-MS/MS Analysis	88
5.1.1	Principle for EI-MS/MS Analysis	88
5.1.2	Operation Mode for EI-MS/MS	88
5.1.3	Advantage of EI-MS/MS	89
5.1.4	Application of EI-MS/MS	90
5.2	Establishment of GC-EI-MS/MS Analytical Method	91
5.2.1	Instrument an Chemicals	92
5.2.2	Analytical Conditions of GC and EI-MS/MS	92
5.2.3	Optimizati`on and Choice of EI-MS/MS	93
5.3	Result and Discussion	99
5.3.1	EI-MS/MS Standard Spectrum of Two PAEs With The Primary Parse	99
5.3.2	Linear Equation and Correlation Coefficient	101
5.3.3	Compare of EI-MS/MS amd EI-MS/MS SIS	104
5.4	Summary	105
Reference 5		106
	Conclusions	107
	Publications during M. Sc. Study	109
	Acknowledgement	111
	Appendix 1 Blacklist of Pollutants Controlled Firstly in Environment in China	113
	Appendix 2 The Use and Harm of Some Primary PAEs	114
	Appendix 3 Name、Molecular Formula、CAS and Molecular Weight of 17 PAEs	115
	Appendix 4 Chracter of PAEs	116

摘 要

酞酸酯类化合物 (Phthalic acid esters, 简称 PAEs) 是塑料制品中不可缺少的一种改性添加剂。过去人们一直认为 PAEs 的毒性低, 因而毫无限制地生产, 但近年来的研究表明, 尽管它们在环境中的残留量不大, 急性毒性不明显, 但具有致突变、致癌和致畸性, 并可混合在食物、空气和其它物质中, 通过消化、呼吸器官和皮肤进入人体, 已对人体健康构成了潜在危害, 故 PAEs 被称为“第二个全球性 PCBs 污染物”。

本学位论文致力于动物内脏, 蔬菜以及塑料橡胶中十几种 PAEs 残留分析的方法研究, 针对不同的样品体系, 建立了以不同溶剂为提取剂的超声提取、Florisil 硅土净化分离、GC-EI/MS 定性定量分析的方法, 同时对 PAEs 的 GC-MS/MS 分析作了初步的探讨。全部内容分为以下五章:

第一章 简要综述了目前国内外 PAEs 环境激素的研究内容。阐述了 PAEs 在大气、水体、泥土和生物体内的污染状况, 并综述了 PAEs 残留的分析方法研究进展, 同时讨论了该课题的研究意义, 并对该课题的后续研究进行了展望。

第二章 开展了动物内脏中 14 种 PAEs 残留的 GC-EI/MS 分析方法研究。初步解析了 PAEs 的 EI/MS 谱图; 优化了样品的前处理条件; 讨论了分析空白值的控制问题; 准确分析了猪肝、鸭肝、鸡肝、牛肝以及猪心、鸭心中 14 种 PAEs 的含量, 证实了 PAEs 环境环境激素在动物内脏中已经有了一定程度的蓄积。

第三章 利用 GC-EI/MS 技术对 16 种 PAEs 化合物的同时分析进行了系统性的研究, 建立了正己烷超声提取, Florisil 硅土柱层析净化, 正己烷/乙酸乙酯 (3/2, v/v) 洗脱的前处理方法。以苯甲酸苄基酯 (BB) 为内标物, 采用内标法的定量方法

对萝卜、茄子、马铃薯、卷心菜、冬瓜五种常见蔬菜中 PAEs 残留进行了分析。为掌握和有效的控制蔬菜等农产品的 PAEs 污染提供了依据。

第四章 开展了塑料橡胶中 13 种常见 PAEs 增塑剂的 GC-EI/MS 的分析方法研究。采用外表法的定量方式，从方法检测限、准确度、精密度和线性范围四个指标考察了分析方法的可靠性。此外，本章特别对含有多种同分异构体的 DINP 的定量分析进行了初步的研究。

第五章 对 PAEs 的 GC-MS/MS 分析方法进行了初步的研究探讨。以 9 种 PAEs 为研究对象，对 MS/MS 各分析参数，如目标物保留时间段、扫描时间、母离子的选择、目标物激发存储水平、碰撞诱导解离电压、共振或非共振 MS/MS 解离方式等进行了探讨和优选，最终建立了 PAEs 的 GC-MS/MS 分析方法。此外，还从响应信号和信噪比两个方面比较了离子存储技术（SIS）和 MS/MS 两种技术的优缺点。

关键词：环境激素；酞酸酯；邻苯二甲酸酯；动物内脏；气相色谱-电子轰击离子源-质谱；动物内脏；蔬菜；塑料橡胶；气相色谱-串联质谱

ABSTRACT

Phthalic acid esters (PAEs) are widely used as plasticizers all over the world. In the past year, people had thought that they were less toxic, but recently, more and more investigations have shown that PAEs are Environmental Incretion. Usually, they combine with the food, the air and other things, coming into body through digestion, respiration or skin and leading to the instability of internal secretions. PAEs are toxic and harmful to hunman, so they are regarded as “The second global PCBs Pollutants” now.

This dissertation focused on the studies of different analytical methods for PAEs in different samples, such as animal innards, vegetables, plastics rubber and so on. The method was as following: extracted with different solvent against different samples, separated by Florisil diatomite, then analyzed by GC-EI/MS SIM. Furthermore, the analytical methods of PAEs by GC-MS/MS was discussed in this thesis preliminarily.

The first chapter, simply introduced the study of PAEs Environmental Incretion in China and abroad, which including the Pollution level of PAEs in different areas and the analytical method of PAEs. Finally, the plan of this dissertation as well as the outlook of the subject was also interpreted.

The second chapter, GC-EI/MS was applied to the determine of 14 PAEs simultaneously in animal innards. Firstly, the structures of PAEs fragments and their EI/MS rupture mechanisms were parsed. Then, the different parameters such as the extractant, the eluent and proportion of eluent were optimized during the pretreatment process., at the same time ,the problem of analytical blank was dissussed. Finally, PAEs were analyzed in six animal innards,

such as pork liver, duck liver, chicken liver, beef liver and so on, confirming that PAEs have been accumulated in animal innards

The third chapter, an analytical method was developed for the simultaneous determination of 16 PAEs in vegetables by GC-EI/MS. PAEs were extracted with hexane in an ultrasonic bath and cleaned up on a Florisil column, then were determined by GC-EI/MS with Benzyl benzoate (BB) as internal standard. At last, the radish, brinjaul, potato, cabbage and wax gourd were analyzed, providing a effective measure for the control of PAEs pollution in vegetables.

The four chapter, developing a GC-EI/MS method for simultaneous determination of 13 PAEs in plastics rubber with external standard method in quantitative. The recoveries, limit of detection, precision and linear range were investigated to pledge the reliability. Furthermore, the quantitative problem of DINP with the isomers was dissussed especially

The fiver chapter, the analytical methods of PAEs by GC-MS/MS was discussed preliminarily in this thesis. Take 9 PAEs for example, several parameters for MS/MS such as scan time, parent ion, excitation storage level, CID voltage, the model of resonant and nonresonant and so on were optimized. Finally, the analytical method of 9 PAEs with GC-MS/MS was established. Furthermore, the MS/MS and SIS were compared in Sensitivity and S/N.

Key Words: Environmental Incretion, Phthalic acid esters, PAEs, GC-EI/MS, animal innards, vegetables, plastics rubber, GC-MS/MS

Degree papers are in the "[Xiamen University Electronic Theses and Dissertations Database](#)". Full texts are available in the following ways:

1. If your library is a CALIS member libraries, please log on <http://etd.calis.edu.cn/> and submit requests online, or consult the interlibrary loan department in your library.
2. For users of non-CALIS member libraries, please mail to etd@xmu.edu.cn for delivery details.

厦门大学博硕士论文摘要库