





# 农药残留高通量检测技术

第一卷 （植物源产品）

**High-Throughput Analytical Techniques for  
Multi-Classes and Multi-Kinds of Pesticide Residues  
Volume I （For Plant Origin）**

庞国芳 等著

Editor-in-chief Guo-Fang Pang

科学出版社

北 京

## 内 容 简 介

本书分为两卷共 11 章。第 1~10 章分别综述近 20 年 10 类不同食用农产品中农药残留样品制备技术和检测技术研究进展,重点介绍作者团队近年来研究开发的 10 项同时测定 400~500 种农药残留的高通量样品制备技术和检测技术。这些技术形成了一个可检测世界常用 1000 多种农药残留的高通量分析方法体系。第 11 章介绍作者团队建立的世界常用 1000 多种农药化学污染物在 GC-MS、GC-MS/MS 和 LC-MS/MS 等不同色谱-质谱条件下的数万份质谱参数数据库。

本书核心技术居国际农药残留分析领域的前沿,其研究成果具有前瞻性、创新性和实用性。可作为大学教学参考书,也可供从事食品安全、农业环境保护及农药开发利用等技术研究与应用的专业技术人员参考。

### 图书在版编目(CIP)数据

农药残留高通量检测技术. 第一卷 / 庞国芳等著. —北京:科学出版社,2012

ISBN 978-7-03-036462-3

I. ①农… II. ①庞… III. ①农药残留量分析 IV. ①X592.02

中国版本图书馆 CIP 数据核字(2013)第 010373 号

责任编辑:杨 震 刘 冉 / 责任校对:宋玲玲 张怡君 刘小梅

责任印制:钱玉芬 / 封面设计:王 浩

科学出版社出版

北京东黄城根北街 16 号

邮政编码:100717

<http://www.sciencep.com>

北京通州皇家印刷厂印刷

科学出版社发行 各地新华书店经销

\*

2012 年 12 月第 一 版 开本:889×1 194 1/16

2012 年 12 月第一次印刷 印张:43 1/2

字数:1 230 000

定价:196.00 元(第一卷)

(如有印装质量问题,我社负责调换)

## 《农药残留高通量检测技术》编委会

主 编 庞国芳

副主编 范春林 曹彦忠 刘永明

编 委 (以姓氏笔画为序)

王明林 方晓明 石志红 刘永明 杨 方

范春林 季 申 庞国芳 莫汉宏 曹彦忠

常巧英 谢丽琪 靳保辉 潘国卿 薄海波

## **Editorial Board**

**Editor-in-chief** Guo-Fang Pang

**Deputy Editor-in-chief** Chun-Lin Fan Yan-Zhong Cao Yong-Ming Liu

**Editorial Board Members** (In order of Chinese surname strokes)

Ming-Lin Wang Xiao-Ming Fang Zhi-Hong Shi

Yong-Ming Liu Fang Yang Chun-Lin Fan

Shen Ji Guo-Fang Pang Han-Hong Mo

Yan-Zhong Cao Qiao-Ying Chang Li-Qi Xie

Bao-Hui Jin Guo-Qing Pan Hai-Bo Bo

# 《农药残留高通量检测技术》各章研究者/著者

## 1 水果蔬菜中农药化学品多组分残留检测技术

庞国芳 范春林 方晓明 曹彦忠 李 岩 曹 静

## 2 粮谷中农药化学品多组分残留检测技术

刘永明 庞国芳 范春林 常巧英 陈 辉 吴艳萍 李 金

## 3 果蔬汁和果酒中农药化学品多组分残留检测技术

庞国芳 范春林 谢丽琪 李 岩 靳保辉 石志红

## 4 茶叶中农药化学品多组分残留检测技术

庞国芳 曹彦忠 郑书展 范春林 胡雪艳 姚翠翠 莫汉宏

## 5 食用菌中农药化学品多组分残留检测技术

庞国芳 范春林 薄海波 王明林 常巧英 王雯雯 纪欣欣

## 6 植物中药材中农药化学品多组分残留检测技术

庞国芳 季 申 范春林 常巧英 石志红 黄 韦 毛秀红

## 7 动物组织中农药化学品多组分残留检测技术

曹彦忠 庞国芳 常巧英 张进杰 李学民 贾光群

## 8 蜂蜜中农药化学品多组分残留检测技术

范春林 庞国芳 连玉晶 刘亚风 赵淑军 康 健

## 9 水产品中农药化学品多组分残留检测技术

范春林 庞国芳 杨 方 薄海波 林 洪 王明林 郑 锋

## 10 牛奶和奶粉中农药化学品多组分残留检测技术

范春林 庞国芳 潘国卿 郑书展 李 岩 郑军红 莫汉宏

## 11 农药化学品多组分残留质谱分析特征参数基础研究

庞国芳 范春林 常巧英 曹彦忠 刘永明 连玉晶 赵淑军 李 岩  
郑 锋 郑军红 王雯雯 曹 静 纪欣欣 姚翠翠 康 健

# List of Contributors

- 1 Analytical Techniques for Multi-Classes and Multi-Kinds of Pesticide Residues and Chemical Pollutants in Fruit and Vegetable**  
Guo-Fang Pang Chun-Lin Fan Xiao-Ming Fang Yan-Zhong Cao Yan Li Jing Cao
- 2 Analytical Techniques for Multi-Classes and Multi-Kinds of Pesticide Residues and Chemical Pollutants in Grain**  
Yong-Ming Liu Guo-Fang Pang Chun-Lin Fan Qiao-Ying Chang Hui Chen Yan-Ping Wu Jin Li
- 3 Analytical Techniques for Multi-Classes and Multi-Kinds of Pesticide Residues and Chemical Pollutants in Fruit Juice, Vegetable Juice and Fruit Wine**  
Guo-Fang Pang Chun-Lin Fan Li-Qi Xie Yan Li Bao-Hui Jin Zhi-Hong Shi
- 4 Analytical Techniques of Multi-Classes and Multi-Kinds of Pesticide Residues and Chemical Pollutants in Tea**  
Guo-Fang Pang Yan-Zhong Cao Shu-Zhang Zheng Chun-Lin Fan Xue-Yan Hu  
Cui-Cui Yao Han-Hong Mo
- 5 Analytical Techniques for Multi-Classes and Multi-Kinds of Pesticide Residues and Chemical Pollutants in Edible Fungi**  
Guo-Fang Pang Chun-Lin Fan Hai-Bo Bo Ming-Lin Wang Qiao-Ying Chang  
Wen-Wen Wang Xin-Xin Ji
- 6 Analytical Techniques for Multi-Classes and Multi-Kinds of Pesticide Residues and Chemical Pollutants in Chinese Medicinal Material of Plant Origin**  
Guo-Fang Pang Shen Ji Chun-Lin Fan Qiao-Ying Chang Zhi-Hong Shi Wei Huang  
Xiu-Hong Mao
- 7 Analytical Techniques for Multi-Classes and Multi-Kinds of Pesticide Residues and Chemical Pollutants in Animal Tissues**  
Yan-Zhong Cao Guo-Fang Pang Qiao-Ying Chang Jin-Jie Zhang Xue-Min Li Guang-Qun Jia
- 8 Analytical Techniques of Multi-Classes and Multi-Kinds of Pesticide Residues and Chemical Pollutants in Honeys**  
Chun-Lin Fan Guo-Fang Pang Yu-Jing Lian Ya-Feng Liu Shu-Jun Zhao Jian Kang
- 9 Analytical Techniques for Multi-Classes and Multi-Kinds of Pesticide Residues and Chemical Pollutants in Aquatic Products**  
Chun-Lin Fan Guo-Fang Pang Fang Yang Hai-Bo Bo Hong Lin Ming-Lin Wang Feng Zheng
- 10 Analytical Techniques for Multi-Classes and Multi-Kinds of Pesticide Residues and Chemical Pollutants in Milk and Milk Powder**  
Chun-Lin Fan Guo-Fang Pang Guo-Qing Pan Shu-Zhan Zheng Yan Li  
Jun-Hong Zheng Han-Hong Mo
- 11 Basic Research on Characteristic Parameters of Chromatography-Mass Spectrometry for Multi-Classes and Multi-Kinds of Pesticide Residues and Chemical Pollutants**  
Guo-Fang Pang Chun-Lin Fan Qiao-Ying Chang Yan-Zhong Cao Yong-Ming Liu  
Yu-Jing Lian Shu-Jun Zhao Yan Li Feng Zheng Jun-Hong Zheng Wen-Wen Wang  
Jing Cao Xin-Xin Ji Cui-Cui Yao Jian Kang

# 序

目前,世界各国对食用农产品中农药化学品残留限量提出了越来越严格的要求,要求检测的农药种类越来越多,农药最大残留限量(MRL)标准越来越低,即国际食用农产品贸易准入门槛越来越高。如日本 2006 年实施的农产品“肯定列表制度”,规定了“暂定限量标准”51 392 条,涉及 264 种食用农产品和 734 种农业化学品,成为目前世界上食用农产品中最严格的农业化学品残留限量管理法规,几乎覆盖了我国现在种植养殖的所有农产品,对我国食用农产品的出口有重要影响,对我国农业化学品残留检测技术研究,既是巨大的挑战,又是重大的机遇。因此,保障国家食品安全,确保我国经济安全运行,不断破解先进国家的技术措施,是我国一项长期的战略任务。

庞国芳科研团队率先抓住食品安全战略发展研究热点,主动迎接挑战,基本与日本“肯定列表制度”研究在同一时期,对 10 类不同食用农产品中多类别多品种的农药残留检测技术进行系统研究,开发出 10 项一次样品制备,可同时提取、分离、富集和测定 400~500 种农药残留的高通量样品制备技术和检测技术。这些技术分别适用于水果蔬菜、粮谷、果蔬汁和果酒、茶叶、食用菌、植物中药材、动物组织、蜂蜜、水产品、牛奶和奶粉等 10 类 60 多种食用农产品中农药多残留的同时检测,形成了一个可检测世界常用 1000 多种农药化学品残留的高选择性、高灵敏度、高分辨率和高通量分析方法体系,并完成了标准化,使我国农药多残留检测技术与世界先进技术接轨,在同时检测的化学品种类和数量上,居国际领先地位。

这部著作是庞国芳科研团队近 30 年从事农药残留检测技术理论与应用研究的结晶,是心无旁骛,长期刻苦攻关、不懈攀登的硕果,这项研究成果具有三个方面的技术创新:

第一,对世界常用 1000 多种农药化学品的气相色谱-(串联)质谱和液相色谱-(串联)质谱特征进行了系统研究,构建了拥有数万份质谱图的数据库,奠定了研发高通量检测技术的理论基础。

第二,集成加速溶剂萃取、高速匀质提取、固相萃取和凝胶渗透等先进前处理技术,攻克了将 1000 多种含量十亿分之几的农药残留从 10 多类 60 余种农产品中有效提取出来,并将大量共萃取干扰物有效分离的一系列技术难题,开发了居国际先进水平的高通量样品前处理技术。

第三,率先研究开发了色谱-质谱按时段分组检测新技术,将化学性质和保留时间相近的农药化学品依次分成若干组,提高了方法的选择性;将每组农药按出峰顺序,细分时段检测,提高了方法的灵敏度;对目标农药选择离子进行优化,降低噪声干扰,提高了方法的分辨率,实现了 500 种农药残留可同时检测,开发出国际领先的高通量样品检测技术,同时检测的农药品种数居国际领先地位。比传统单残留方法提高工作效率数百倍,形成了一个自动化水平比较高的农药多残留分析方法体系。

这项研究具有三方面的重要意义:

第一,具有重要的战略意义。在世界经济一体化进程中,国际竞争越来越激烈。世界先进国家及地区利用技术壁垒保护本国利益,已取得显著成效。早在 2006 年我国因先进国家及地区技术壁垒造成的经济损失就高达 1000 多亿美元,国外技术壁垒已成为我国外贸发展的主要障碍,食用农产品是我国遭遇国外农药残留技术壁垒比较多的商品,而这些技术方法的研究,将成为破解世界先进国家及地区技术壁垒的有力武器,这也反映出发展中的中国综合国力的提升。

第二,具有重要的现实意义。农药最大残留限量标准不仅是食品安全的标准,也是国际贸易的准入门槛,世界各国对食品安全高度重视。食用农产品国际贸易农药残留限量门槛越设越多、越设越严的严峻形势,国际贸易快节奏、高效率的发展,必然对检测技术的高选择性、高灵敏度、高分辨率、高通量提出更高的要求和挑战,这些多残留检测技术基本满足了这些要求。

第三,具有重要的学术价值。农药化学品高通量检测技术是当前各国同行的热点研究课题,是具有很难度的课题。这项研究实现了与国际先进技术的接轨,同时在检测的品种方面,超过了先进国

家的同类技术。研究论文在美国、荷兰、德国、英国等国际期刊上发表,得到了国际同行的认可。在国际会议上的报告也得到同行赞许,扩大了我国在残留分析和食品痕量分析化学领域的国际影响,促进了该领域的技术进步。



中国工程院院士

2012年10月18日

## Foreword

At present, countries from all over the world have set forth more and more stringent requirements for chemical contaminants in edible agricultural products, and there are more and more pesticide varieties requiring determination, whereas the maximum residue limit (MRL) for pesticides is getting lower and lower, i. e. the threshold of access for international edible agricultural products is getting higher and higher. For instance, “Positive List” system implemented by Japan in 2006 stipulated 51 392 “Interim Limit Standards” involving 264 edible agricultural products and 734 agricultural chemical contaminants, being the strictest regulatory law of pesticide and veterinary drug residues in edible agricultural products in the present world and covering almost all agricultural products currently planted or cultivated in our country, which poses influence of great magnitude on export of edible agricultural products of our country. This is both a huge challenge and an important opportunity for the study of pesticide and veterinary drug residue analytical techniques of our country. Therefore, it is a long-term strategic task for our country to protect national food safety, ensure the safe operation of our economy and constantly crack the technical barriers of advanced countries.

Guo-Fang Pang’s team has taken the lead in capturing the research hot-spot of strategic development of food safety and displayed great initiative in meeting the challenge. Almost contemporary to the research of Japan’s “Positive List”, they conducted a systematic study on analytical techniques for multi-classes and multi-kinds pesticide residues in 10 categories of different edible agricultural products and developed 10 high-throughput sample preparation techniques and high-throughput analytical techniques for simultaneous extraction, separation, enrichment and determination of 400-500 pesticide residues with one-time sample preparation. These techniques are respectively applied in determination of pesticide multiresidues in over 60 edible agricultural products of 10 categories such as fruits and vegetables, grains and cereals, fruit and vegetable juices and fruit wines, teas, edible fungi, plant and herbal medicines, animal tissues, honeys, aquatic products, milk and milk powder, etc., forming an analytical method system of high selectivity, high sensitivity, high resolution and high throughput for determination of over 1000 world commonly-used pesticides and chemical contaminants residues, based on which, standardization has been completed, enabling pesticide multiresidue techniques of our country to be integrated with those of advanced countries and occupying the international leading position in terms of varieties and quantities of chemical contaminants simultaneously analyzed.

This book is the fruit from Guo-Fang Pang’s team, who have been engaged in the research of pesticide residue analytical techniques over the past 30 years or so, combining their theories with applications, as well as the fruit from the team who have been whole-heartedly committed to their duties without any other distractions, stormed one stronghold after another and kept climbing uphill towards the summit. This research is of technical innovations in the following three aspects:

Firstly, a systematic study has been conducted on the characteristics of GC-MS/MS and LC-MS/MS for over 1000 world commonly used pesticide chemical contaminants, and a data bank with thousands of mass spectrograms has been established, laying a theoretical foundation for developing the high-throughput analytical technique.

Secondly, advanced sample preparation techniques such as accelerated solvent extraction, high-speed homogenous extraction, solid-phase extraction, gel permeation chromatography, etc. have been integrated, a series of technical hurdles have been overcome like extracting over 1000 pesticide residues with the content of ppb level from over 60 agricultural products of 10-plus categories and effectively separating big quantities of co-extracting interfering matters, and the high-throughput sample preparation techniques of internationally advanced level have been developed.

Thirdly, Guo-Fang Pang's team have taken the lead in studying and developing a new technique of determination per time frames and groups for chromatography and mass spectrometry and sequentially divided pesticide chemical contaminants of chemical properties and retention time that are close to each other into multiple groups, thus the selectivity of the method has been raised; each group of pesticides was determined per time frame in accordance with the peaking sequence, thus the sensitivity of the method has been raised; the ions were chosen to optimize target pesticides to lower the noise interference, thus the method resolution has been increased, and simultaneous determination of 500 pesticide residues has been realized, whereas the high-throughput sample analytical technique of internationally advanced level has been developed, and in the meantime, the number of pesticide varieties simultaneously determined occupies a leading position in the world. The working efficiency by this method has increased hundreds of times compared with that by the conventional single-residue method. Based on what is mentioned above, a pesticide multiresidue analytical method system with relatively high automation has taken shape.

This research is of great significance in the following three aspects:

Firstly, it is of strategic importance. In the process of globalization of world economy, international competition is getting more and more cut-throat. Developed countries in the world have been protecting the interests of their own countries by setting up technical barriers and obtained remarkable results. As early as in 2006, our country suffered economic loss up to 100 billion US dollars as a result of foreign technical barriers, and foreign technical barriers have become the main obstacles to our foreign trade development. Edible agricultural products take up relatively the most majority of encountering foreign technical barriers of pesticide residues, so the research of such techniques will turn into powerful weapons for removing the technical barriers of world advanced countries, which also reflects the increase of the comprehensive national strength of developing China.

Secondly, it is of realistic importance. Pesticide maximum residue limit (MRL) is not only the standard for food safety, but also the threshold of access for international trade. Countries from all over the world attach great attention to food safety, so there are more and more pesticide residue limit thresholds for international trade of edible agricultural products and stricter and stricter limits; the international trade rhythm is getting faster and faster, and efficiency is getting higher and higher. Such circumstances necessarily call for higher standards and greater challenges for the high sensitivity, high resolution, high selectivity and high throughput of analytical methods, whereas these multiresidue analytical techniques have basically met all these requirements.

Thirdly, it is of academic importance. Pesticide chemical contaminants high-throughput analytical techniques are the topics of hotspot research by our counterparts from all over the world, which is very hard to tackle. This research has realized the integration with the international advanced techniques, and in the meantime exceeded the similar techniques of advanced countries in terms of the number of pesticide varieties simultaneously determined. The research papers were published on fa-

---

mous international journals in countries such as USA, UK, Holland, Germany, etc. and have gained recognition by our international counterparts. In addition, our presentations made at international meetings were very well received by our colleagues from all over the world, which helped our country to exert international influence in the arenas of international residual analysis and trace analytical chemistry and has induced the technological progress of the said area.

Fu-Sheng Wei

Academician of the Chinese Academy of Engineering

October 18, 2012

# 前 言

本书是作者团队近 30 年从事食用农产品农药残留检测理论与实践研究的总结,主要介绍了水果、蔬菜、粮谷、果蔬汁和果酒、茶叶、食用菌、植物中药材、动物组织、蜂蜜、水产品、牛奶和奶粉等产业的发展 and 国际贸易对农药残留检测技术的需求,综述了相应样品制备技术和检测技术进展,重点阐述了作者团队在农产品农药残留检测技术领域的研究成果。

在撰写本书的过程中,作者团队检索了近 20 年(1991~2010 年)的 15 种国际期刊\*,关于食用农产品中农药残留检测技术的 SCI 论文 3505 篇,源于五大洲 72 个国家和地区,其中欧洲 33 个国家 1942 篇,美洲 13 个国家 852 篇(北美洲 3 个国家 756 篇,南美洲 10 个国家 96 篇),亚洲 18 个国家和地区 641 篇,大洋洲 2 个国家 38 篇,非洲 6 个国家 32 篇。按论文数量对 72 个国家和地区进行排序,其中排名前 20 位的国家依次是西班牙、美国、中国、意大利、英国、加拿大、日本、德国、法国、比利时、希腊、荷兰、巴西、印度、瑞士、爱尔兰、葡萄牙、澳大利亚、捷克和波兰。通过对排名前 20 位的国家按前 10 年(1991~2000 年)和后 10 年(2001~2010 年)的发展历程进行比较发现,前 10 年排名前 3 位的是美国、西班牙和英国,中国排在第 13 位,而后 10 年排名前 3 位的国家是西班牙、中国和美国。我国由前 10 年的第 13 位,跃升为后 10 年的第 2 位。这充分表明,从论文数量来看,我国在食用农产品农药残留检测领域,已跨入世界大国行列。

就食用农产品农药残留样品制备技术而论,3505 篇论文涉及样品制备技术 89 种。按论文数量,排名前 20 位的技术是固相萃取(SPE)、液液萃取(LLE)、基质固相分散萃取(MSPDE)、超临界流体萃取(SFE)、凝胶渗透色谱(GPC)、衍生化(Derivatisation)、QuEChERS 技术、加速溶剂萃取(ASE)、固相微萃取(SPME)、免疫亲和色谱(IAC)、微波辅助萃取(MAE)、液相色谱(LC)、分散固相萃取(DSPE)、索氏提取(SE)、搅拌棒吸附萃取(SBSE)、单滴微萃取(SDME)、薄层色谱(TLC)、超声辅助萃取(UAE)、半透膜净化(SPMD)和分散液液微萃取(DLLME)。对前 10 年和后 10 年发展历程进行比较发现,20 年一直处于领先地位的技术是 SPE、LLE,分别排第 1 位和第 2 位。排位上升最快的技术有:基质固相分散萃取(MSPDE)由前 10 年的第 6 位上升到后 10 年的第 3 位;加速溶剂萃取(ASE),由前 10 年的第 15 位上升到后 10 年的第 8 位。地位基本稳定的技术为:凝胶渗透色谱(GPC)、衍生化(Derivatisation)。新涌现的技术是 QuEChERS 技术,后 10 年才出现已位居第 7 位。此外还有单滴微萃取(SDME)、搅拌棒吸附萃取(SBSE)、半透膜净化(SPMD)、分散液液微萃取(DLLME)等,分别排第 16、18、19、20 位。通过对比研究发现,就样品制备技术而论,简单、快速和高效是样品制备技术研究开发的总趋势。在本书中,对于排名前 20 位的样品制备技术应用进展,将在对应的各有关章节中一一进行介绍。对于没有排名前 20 位的新出现的样品制备技术,也有适当介绍。对于作者团队研发的高通量样品制备技术,将分别在相应各章中进行重点介绍。

就食用农产品农药残留检测技术而论,3505 篇论文涉及检测技术 204 种,按论文总量排名前 20 位的技术是:气相色谱-质谱(GC-MS)、液相色谱-串联质谱(LC-MS/MS)、液相色谱-紫外检测(LC-UV)、气相色谱-电子捕获检测(GC-ECD)、液相色谱-质谱(LC-MS)、液相色谱-荧光检测(LC-FLD)、酶联免疫(ELISA)、液相色谱-二极管阵列检测(LC-DAD)、气相色谱-氮磷检测(GC-NPD)、气相色谱-串联质谱(GC-MS/MS)、传感器(Sensor)、气相色谱-火焰光度检测(GC-FPD)、液相色谱-飞行时间质谱(LC-

---

\* 15 种国际期刊包括:Chromatographia, Journal of AOAC International, International Journal of Environmental Analytical Chemistry, Food Additives and Contaminants, Journal of Agricultural and Food Chemistry, Journal of Separation Science, Rapid Communications in Mass Spectrometry, Food Chemistry, Analyst, Talanta, Analytical and Bioanalytical Chemistry, Analytica Chimica Acta, Journal of Chromatography A, Analytical Chemistry 和 TrAC-Trends in Analytical Chemistry。

QTOF)、薄层色谱(TLC)、毛细管电泳(CE)、酶免疫(EIA)、气相色谱-氢火焰离子化检测(GC-FID)、毛细管电泳-紫外检测(CE-UV)、液相色谱-电化学检测(LC-ED)、气相色谱-离子阱质谱法(GC-ITD)和免疫分析(IA)。对前10年和后10年发展历程进行比较发现:发展最快的技术是LC-MS/MS,由前10年的第9位上升到后10年的第1位;GC-MS/MS由前10年的第19位上升至后10年的第8位;传感器(Sensor)由前10年的第17位上升至后10年的第10位;后10年新产生的技术是TOF-MS、Orbitrap等;排位稳定的技术是GC-MS、ELISA、LC-MS、GC-ECD、LC-DAD、CE等;排位下降最快的技术是LC-UV,由前10年的第1位,下降至后10年的第6位;呈下降趋势的技术是LC-FLD,由前10年的第4位下降至后10年的第7位;GC-NPD由前10年的第7位下降至后10年的第11位。对比研究发现,就检测技术而论,准确、快速和高通量检测技术是研究开发的总趋势。在本书中,对排前20位的样品检测技术应用进展,将在对应的各有关章节中一一进行介绍,对于没有排前20位的新出现的样品检测技术,也有适当介绍。对于作者团队研发的高通量检测技术,将分别在相应各章中进行重点介绍。

值得特别提出的是,在过去20年最引人瞩目的技术是GC-MS/MS和LC-MS/MS,上述15个科学技术杂志前10年(1991~2000年)发表的色谱-质谱检测技术论文是339篇,而到后10年(2001~2010年)则达到了1018篇,后10年约是前10年的3倍。这充分说明,在食用农产品检测技术方面,色谱-质谱检测技术已迎来了空前发展的时期。我国这一领域科技工作者紧跟这一技术的前进步伐,使我国在这一领域由前10年的第14位,跃升到后10年的第2位,为我国在这一领域国际地位的提升,作出了杰出贡献。作者科研团队的实验室,在前10年还没有质谱分析仪器,在后10年感受到研究色谱-串联质谱的重要性和紧迫感,决定借用仪器从事食用农产品中农药化学品多组分残留高通量检测技术研究。2000~2008年,经过了四个研究阶段:第一阶段(2000~2002年)突破传统思路,探索按时段分组检测新技术,解决蜂蜜、果汁、果酒三种基质中304种农药多残留同时检测的一系列技术难题;第二阶段(2003~2005年)力戒浅尝辄止,加大研究深度和广度,除蜂蜜、果汁、果酒外,又新增水果、蔬菜、粮谷和动物组织,共七种基质组配,突破检测468种;第三阶段(2005~2006年)独辟蹊径,使研究水平再上一个台阶,突破检测768种;第四阶段(2006~2008年)再接再厉,初步形成农产品食品中农药残留检测体系,检测品种突破了1000种。

在这10年的研究中,作者所在团队评价了世界常用1000多种农药的GC-MS、GC-MS/MS、LC-MS/MS、TOF-MS和Orbitrap质谱特征,建立了上述五种色谱-质谱技术在不同条件下的质谱数据库,为实现农药多组分残留高通量检测奠定了理论基础。随后,研究建立了世界常用1000多种农药在水果、蔬菜、粮谷、果蔬汁、果酒、茶叶、食用菌、植物中药材、动物组织、蜂蜜、水产品、牛奶和奶粉等12类63种农产品基质中的高通量样品制备技术和检测技术,实现了一次制备样品,可同时检测400种以上多组分残留的高通量检测技术,达到国际先进水平。在用一种方法同时检测的农药品种数量方面,居国际领先地位。更为庆幸的是,2008年第十一届全国人民代表大会第一次会议《政府工作报告》中明确提出,要完成7700多项食品、药品和其他消费品安全国家标准制定修订工作,由于作者团队在这一领域长期潜心研究,有幸承担了其中79项检测技术国家标准的研究,使这些检测技术实现了标准化,并已广泛应用,在保障相关食用农产品质量的提高,促进我国对外贸易发展方面作出了贡献。同时,也引起国际AOAC组织和同行的重视,扩大了我国在这一领域的国际影响。

本书力求将这一领域国内外先进技术发展和近年来作者团队的系列高通量检测技术研究成果呈现给大家,但水平有限,不妥之处在所难免,敬请广大读者批评指正。



中国工程院院士  
2012年9月3日

## Preface

This book is a summary of the research on analysis of pesticide residues in edible agricultural products in terms of theory and practice by the author's team who have been involved in this field for nearly 30 years. The chapters are designed per the categories of edible agricultural products such as fruits and vegetables, grains and cereals, fruit and vegetable juices, fruit wines, teas, edible fungi, Chinese herbal medicines, animal tissues, honeys, aquatic products, milk and milk power, etc., each chapter of which deals briefly with the industrial development and the requirements for such techniques in the international trade, summarizes the development of corresponding sample preparation techniques and analytical techniques and lays an emphasis on the detailed description of the research results of high throughput analytical techniques in agriculture products by the author's team.

In the process of writing this book, the author's team searched 15 international influential journals\* that have been published for the past 20 years or so (1991-2010), and found there are 3505 SCI papers on analytical techniques for pesticide residues in edible agricultural products from 72 countries (regions) across the five continents, among which 1942 papers are from 33 countries in Europe, 852 papers from 13 countries from America, 641 papers from 18 countries (regions) in Asia, 38 papers from 2 countries in Oceania and 32 papers from 6 countries in Africa. Putting the 72 countries and regions in sequential order per paper quantities, countries that rank the top 20 are Spain, USA, China, Italy, UK, Canada, Japan, Germany, France, Belgium, Greece, Holland, Brazil, India, Switzerland, Ireland, Portugal, Australia, Czech and Poland. A comparison of countries that rank the top 20 per the first 10 years (1991-2000) and the last 10 years (2001-2010) has found that countries that rank the top 3 in the first 10 years are USA, Spain and UK, with China in 13<sup>th</sup> place, whereas countries that rank the top 3 in the last 10 years are Spain, China and USA. Our country has jumped to Rank No. 2 in the last 10 years from the 13<sup>th</sup> place in the first 10 years. This fully demonstrates that our country, in terms of paper quantities, has already run neck and neck with the big countries in the world in the field of inspection of pesticide residues in edible agricultural products.

Concerning sample preparation techniques of pesticide residues in edible agricultural products, there are 3505 papers involving 89 sample preparation techniques. In terms of paper quantities, the top 20 techniques are SPE, LLE, MSPDE, SFE, GPC, Derivatisation, QuEChERS, ASE, SPME, IAC, MAE, LC, DSPE, SE, SBSE, SDME, TLC, UAE, SPMD and DLLME.

A comparison of the techniques per the first 10 years and the last 10 years has found that techniques that have been in the leading position for the past 20 years are SPE and LLE, which ranks 1<sup>th</sup> and 2<sup>nd</sup>. Techniques that rise the fastest are MSPDE, which rose to No. 3 in the last 10 years from No. 6 in the first 10 years, and ASE rose to No. 8 in the last 10 years from No. 15 in the first 10 years. Techniques that remain relatively stable are GPC and Derivatisation, and the newly emerged is QuEChERS, which occupied the 7<sup>th</sup> place since its emergence in the last 10 years. In addition, SDME,

---

\* Fifteen international influential journals: *Chromatographia*, *Journal of AOAC INTERNATIONAL*, *International Journal of Environmental Analytical Chemistry*, *Food Additives and Contaminants*, *Journal of Agricultural and Food Chemistry*, *Journal of Separation Science*, *Rapid Communications in Mass Spectrometry*, *Food Chemistry*, *Analyst*, *Talanta*, *Analytical and Bioanalytical Chemistry*, *Analytica Chimica Acta*, *Journal of Chromatography A*, *Analytical Chemistry* and *Trac-Trends in Analytical Chemistry*.

SBSE, SPMDs, and DLLME respectively rank No. 16, No. 18, No. 19 and No. 20. A comparative study found that concerning sample preparation techniques, simple, quick and high efficiency are the general tendencies for the study and development of sample preparation techniques. In this book, an introduction is made item by item to the applications and prospects of sample preparation techniques that rank the top 20 in each of the corresponding chapters. And a brief survey is also made where appropriate for the newly emerged sample preparation techniques that are out of the top 20. Regarding the high throughput sample preparation techniques developed by the author's team, an elaborate introduction is respectively made in the corresponding chapters.

Concerning pesticide residue analytical techniques for edible agricultural products, there are 3505 papers involving 204 analytical techniques. Techniques that rank the top 20 in terms of paper quantities are GC-MS, LC-MS/MS, LC-UV, GC-ECD, LC-MS, LC-FLD, ELISA, LC-DAD, GC-NPD, GC-MS/MS, Sensor, GC-FPD, LC-Q-TOF-MS, TLC, CE, EIA, GC-FID, CE-UV, LC-ED, GC-ITD and IA.

A comparison of the technique development per the first 10 years and the last 10 years has found that the technique that developed the fastest is LC-MS/MS, which rose to Rank No. 1 in the last 10 years from No. 9 in the first 10 years; GC-MS/MS rose from No. 19 in the first 10 years to No. 8 in the last 10 years; Sensors jumped from No. 17 in the first 10 years to No. 10 in the last 10 years; the newly emerged techniques in the last 10 years are LC-Q-TOF-MS, LTQ-Obitrap, etc.; techniques that are relatively stable are GC-MS, ELISA, LC-MS, GC-ECD, LC-DAD, CE, etc.; techniques that dropped the fastest are LC-UV, which dropped from Rank No. 1 in the first 10 years to No. 6 in the last 10 years; techniques that have a tendency of dropping are LC-FLD, which dropped from No. 4 in the first 10 years to No. 7 in the last 10 years, GC-NPD from NO. 7 in the first 10 years to No. 11 in the last 10 years. A comparative study found that concerning analytical techniques, accurate, quick and high throughput techniques are the general tendencies for the study and development of analytical techniques. In this book, an introduction is made item by item to the applications and prospects of analytical techniques that rank the top 20 in each of the corresponding chapters. And a brief survey is also made where appropriate for the newly emerged analytical techniques that are out of the top 20. Regarding the high throughput analytical techniques developed by the author's team, an elaborate introduction is respectively made in the corresponding chapters.

What is worth mentioning is that over the past 20 years the most shining techniques are LC-MS/MS and GC-MS/MS. In the above-described 15 scientific journals, there are 339 papers on chromatography-mass spectrometric techniques in the first 10 years (1991-2001), while there are as many as 1018 papers on the same topic published in the last 10 years (2001-2010), which is three times those in the first 10 years for the last 10 years. This fully demonstrates that chromatography-mass spectrometric techniques have entered into an era of unprecedented development in the field of inspection of edible agricultural products. Scientists and technologists of our country devoted to this area are closely keeping pace with this technique and have brought about the great leap of our country from Rank No. 14 in the first 10 years to No. 2 in the last 10 years in the field of pesticide residue analysis.

Looking back to over 10 years ago, the author's team still did not possess a chromatography-mass spectrometer in their own laboratories, but after deliberating the latest development of analytical techniques, they predicted chromatography-mass spectrometric techniques would play a more and more important role in pesticide residue analysis of foodstuffs, feeling a pressing need to study and develop such techniques, so they decided to borrow instruments from outside sources to conduct the research of high throughput multi-grouped residual analytical techniques for pesticide chemical con-