

QuEChERS 方法在茶叶农药残留检测中的应用研究进展

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摘 要: 茶叶的农药残留检测关系到茶叶的质量安全。茶叶样品基质复杂, 干扰物质多, 其样品前处理是农药残留检测过程中耗时最长、工作量最大的部分, 并决定分析方法的准确度和精密度。QuEChERS(quick, easy, cheap, effective, rugged, safe)方法作为一种农药多残留分析的前处理方法, 由于具有快速、简单、廉价、有效、可靠、安全的特点而成为近年来的研究热点。本文在简要介绍 QuEChERS 方法的基础上, 综述了该方法在茶叶农药残留检测中的重要应用, 详细评述了在取样量选择、样品预处理方法、提取剂选择及净化过程等方面对 QuEChERS 方法进行优化改进的研究进展。分析了 QuEChERS 方法在茶叶农药残留检测中存在的问题和不足, 展望了该方法在茶叶农药残留检测中的发展方向, 以期 QuEChERS 方法在茶叶农药残留检测中的完善和发展提供参考。

关键词: QuEChERS; 茶叶; 样品前处理; 农药残留

QuEChERS methodology and its application in pesticide residues determination in tea

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ABSTRACT: The determination of pesticides residues in tea is a critical problem as the quality and safety of tea has become a hot topic. Sample preparation procedures are time-consuming and labor-intensive because of the small quantities of analytes and large amounts of interfering substances in tea which can be co-extracted with analytes and, in most cases, adversely affect the results of an analysis. Additionally, the accuracy and precision of analytical methods mostly depend on the quality of sample preparation procedures. QuEChERS methodology, which stands for “quick, easy, cheap, effective, rugged and safe”, is a streamlined and effective extraction and cleanup approach for the analysis of diverse pesticides residues in food matrices, and has received much concern since its inception. This review mainly introduces QuEChERS methodology and its application in pesticide residues analysis in tea. The optimization processes including sampling, sample preparation, extraction and purification of QuEChERS methodology were reviewed. Furthermore, limitations as well as possible research tendency of QuEChERS methodology have been discussed to provide certain reference for

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the development and improvement of its application in pesticide residues analysis in tea.

KEY WORDS: QuEChERS; tea; sample preparation; pesticide residues

1 引言

茶叶是当今世界三大无酒精饮料之一。我国作为茶树的原产地,不仅是茶叶生产大国,也是茶叶出口大国。2013年,我国茶园面积共计2579千公顷,全国干毛茶总产量为189万吨^[1],均已上升至全球第一位^[2],出口量为33.2万吨,是世界茶叶第二大出口国,占世界茶叶贸易总量的17.8%^[3],其中摩洛哥、日本、美国和欧盟等是我国茶叶出口的主要国家和地区。然而,随着国际贸易竞争的不断加剧以及各国对食品安全要求的提高,近年来以日本和欧盟为代表的茶叶进口国家和地区对茶叶制定了更为严格的农药残留限量标准,且农药残留检测项目不断增多(例如,1999年欧盟关于茶叶中农药残留的限量标准仅有7项,到2012年已多达1135项)^[4],使茶叶的农药残留问题成为我国茶叶出口的瓶颈。因此,建立茶叶中农药的多残留分析方法,寻求检测时间短、灵敏度高、重现性好、操作简单的茶叶农药残留检测技术,加大对我国茶叶中农药残留的监测力度,对于保证食品安全,适应世界贸易市场的需要,避免和减少不必要的农业损失和国际贸易争端等具有重要的理论和实践意义。

样品前处理是农药残留分析的重要步骤。由于茶叶基质的复杂性,传统的茶叶样品前处理技术如索式提取、液-液萃取等较为繁琐,已无法满足现代农药残留分析的需要。近年来出现了一些新型前处理方法,如固相萃取(solid phase extraction, SPE)^[5]、固相微萃取(solid phase microextraction, SPME)^[6]、液相微萃取(liquid phase microextraction, LPME)^[7]、搅拌棒吸附萃取(stir bar sorptive extraction, SBSE)^[8,9]、凝胶渗透色谱(gel permeation chromatography, GPC)^[5]、加速溶剂萃取(accelerated solvent extraction, ASE)^[5]、微波辅助萃取(microwave-assisted extraction, MAE)^[6,10]、基质固相分散(matrix solid phase dispersion, MSPD)^[11]等,这些新方法已在茶叶农药残留分析中得到广泛应用。尽管这些方法高效、快速、安全、简便,对环境污染较少,但存在处理样品尺寸小、使用范围有限^[12]、对目标农药具有一定选择性等问题,无法满足对绝大多数农药同时检测且达到较高分析质量的技术要求。

QuEChERS (quick, easy, cheap, effective, rugged, safe)方法是近年来国际上最新发展起来的一种快速样品前处理技术,因其具有快速(quick)、简单(easy)、便宜(cheap)、有效(effective)、可靠(rugged)、安全(safe)的特点而得名QuEChERS。该方法自提出后就受到农药残留分析人员的重视,正逐渐成为农药残留检测的一个研究热点。本文就

QuEChERS方法及其在茶叶农药残留检测中的应用研究进展进行评述。

2 QuEChERS方法简介

2.1 QuEChERS方法的建立和发展

2002年,QuEChERS方法首次由美国农业部东部地区研究中心首席科学家Lehotay及博士后Anastassiades在意大利罗马举行的第四届欧洲农药残留工作组会议上提出。该方法是在MSPD技术基础上开发的一种针对水果和蔬菜样品中农药残留检测的新型样品前处理方法,其处理过程为:首先,样品粉碎后用乙腈、乙酸乙酯或丙酮等有机溶剂提取,同时加入盐(硫酸镁或氯化钠),以促使溶剂和水相分离;其次,混合体系经过振摇和离心后,取部分有机相与吸附剂混合,利用分散固相萃取净化;最后,有机相与吸附剂的混合物离心后所得上清液被直接用于分析或浓缩或溶剂交换^[13]。该方法仅需几步就可以完成样品的前处理过程,且可分析几十种果蔬中的数百种农药。故此方法一经发布就受到各国农药残留分析人员的广泛关注。此后,为扩大其所适用的基质范围,提高农药回收率,该方法得到不断改进。2005年,Lehotay等^[14,15]提出了缓冲QuEChERS法,即采用含0.1%乙酸的乙腈作为提取液,以无水乙酸钠代替氯化钠作为盐析剂,借助乙酸/乙酸钠缓冲体系控制水相和有机相的酸碱度,提高了百菌清等对碱敏感的农药的回收率;采用优化后的QuEChERS方法进行前处理,气相色谱-质谱(gas chromatography-mass spectrometry, GC-MS)或液相色谱-质谱(liquid chromatography-mass spectrometry, LC-MS)检测,可以同时分析果蔬样品中的229种农药残留,其中206种农药的回收率在90%~110%之间,11种在70%~120%之间,相对标准偏差均小于10%。该方法经过多个权威实验室验证后,于2007年被美国分析化学师协会确定为其官方方法。此后,由Anastassiades提出另外一种缓冲QuEChERS法,即添加离子强度较小的柠檬酸钠和柠檬酸二钠缓冲溶液调节提取过程中溶液的pH,提取液经硫酸镁和氯化钠盐析离心分层,分散固相萃取后采用GC-MS或LC-MS检测^[16]。该方法经验证后成为欧洲标准化委员会的标准方法EN15662。

2.2 QuEChERS方法的优势

与传统方法相比,QuEChERS方法仅需几步即可完成样品的前处理过程,这对农药残留检测来说意义重大,因为每增加一个步骤都有可能引入新的系统误差和随机误差,且增加分析人员的工作量,降低工作效率。QuEChERS方

法的显著优点有^[17]: (1)对多种农药均有较高的回收率,包括大量极性及挥发性农药; (2)稳定性好,精密度和准确度高; (3)可测定含水量较高的样品,有效减少样品基质如叶绿素、油脂、水分等的干扰; (4)样品通量高,每 30~40 min 可完成 10~20 个预先称重样品的检测; (5)溶剂使用量少,且不使用含氯的溶剂,污染小; (6)样品制备过程所需装置简单; (7)操作简便,可由未经大量训练相关技能的人员操作完成; (8)有机溶剂加入容器后立即密封,减少有机溶剂与工作人员的接触机会; (9)分析成本低廉,每 10 g 样品仅需价值约 1 美元的试剂。

2.3 QuEChERS 方法应用现状

基于 QuEChERS 方法的显著优势以及仪器检测技术的不断发展,分析人员不断拓展 QuEChERS 方法的应用领域。目前,QuEChERS 方法除广泛应用于水果和蔬菜等高含水量样品中的农药残留检测外,还被应用于油脂类^[18]、粮谷类^[19]、土壤^[20]、中药材^[21]、动物源食品^[22]等样品中农药残留的检测和牛乳^[23,24]、鸡蛋^[25]、蜂蜜^[26]、肌肉组织^[27]等样品中兽药残留的检测。除此之外,其研究应用领域还包括食品添加剂^[28]、多环芳香烃类^[29]、生物毒素^[30,31]、药物残留^[32]的检测和中药中非法添加物的鉴别^[33]。

3 QuEChERS 方法在茶叶农药残留检测中的应用与优化

3.1 QuEChERS 方法在茶叶农药残留检测中的应用

由于 QuEChERS 方法所具有的诸多优点,分析人员对其在茶叶农药残留检测中的应用也开展了较多研究,并取得了一定进展。黄诚等^[34]用含 0.1% 乙酸的乙腈提取茶叶中的拟除虫菊酯类农药残留,选取 N-丙基乙二胺(primary secondary amine, PSA)、ODSC₁₈ 和石墨化碳黑(graphitized carbon blacks, GCB)进行净化,净化液采用气相色谱-电子捕获检测器分析,所得 8 种农药加标回收率为 78.2%~109.0%,相对标准偏差为 1.5%~7.9%。叶江雷^[35]等建立了 QuEChERS-GC-MS 技术检测茶叶中 47 种农药残留的方法,样品采用乙腈提取,PSA 和 GCB 净化;结果表明,采用该方法检测时,所有农药的加标回收率、精密度、检测限、定量限基本符合日本和欧盟对农药残留“一律标准”的要求。Lozano 等^[36]采用改进的 QuEChERS 方法分析绿茶、红茶和黑茶中的 86 种农药残留,采用加入磷酸三苯酯的乙腈提取,柠檬酸盐缓冲溶液调节 pH,无水氯化钙代替无水硫酸镁除去多余的水分,LC-MS/MS 和 GC-MS/MS 检测;结果表明,86 种农药中大多数农药的回收率都在 70%~120%之间。Zhang 等^[37]采用改进的 QuEChERS 方法分析茶叶中的三唑类杀菌剂残留时,以乙腈为提取溶剂,C₁₈、PSA 和弗罗里硅土净化后,增加了一个液液微萃取的过程,有效减少了基质的干扰,所得农药的回收率在

91%~118%之间。

3.2 QuEChERS 方法在茶叶农药残留检测中的优化

与其他植物源性食品相比,茶叶富含生物碱、茶多酚和色素类化合物,易对检测造成干扰。因此,优化茶叶样品的前处理条件,对降低检测限、提高检测效率尤为重要。在使用 QuEChERS 方法前处理时,通常需优化取样量、提取剂和净化剂的种类及其用量等,以满足农药残留检测的要求。

3.2.1 取样量及样品预处理的优化

QuEChERS 方法最初设计时是针对含水量较高的蔬菜和水果的,其取样量通常为 10 g。对含水量低的茶叶而言,取样量需适当减少,通常为 2 g 或者 5 g^[38-41]。在相同条件下,减小样品的颗粒度可增加其均匀度,使在更小样品规模下的检测成为可能;但样品颗粒太小又会影响离心分离的效果和上清液的吸取。因此,适宜的颗粒度对检测的可行性和有效性尤为重要。研究发现,干燥茶样的颗粒度为 20~50 目较为适宜^[35,39,42];同时,为确保茶叶中的待分析物容易被提取出来,常添加一定量的水进行浸泡^[41-43]。而张新忠等人则认为,对非极性农药而言,干茶样中加水浸泡后提取并不能改善对此类农药的提取效果,反而会增加咖啡碱等水溶性杂质的浸出而加大后续净化的难度^[44]。由此可见,茶叶样品的预处理过程中是否加水,主要取决于目标农药极性的强弱。检测极性农药时可采用加水浸泡的预处理方式,以提高农药的回收率;而对非极性农药而言,在保证较高回收率的基础上,可直接采用有机溶剂提取,以减少水溶性杂质的浸出。

3.2.2 提取剂的选择

提取剂的选择是开发多残留分析方法的关键因素之一,其选择合理与否直接影响农药回收率的高低及后续净化的难易程度。QuEChERS 方法中常用的提取溶剂包括乙腈、乙酸乙酯和丙酮。和乙酸乙酯与丙酮相比,采用乙腈提取茶叶中的农药时,共萃物较少,同时加入氯化钠,通过盐析作用,易于实现乙腈与水的分离。因此,乙腈是采用 QuEChERS 方法分析茶叶农药残留时最常用的提取溶剂^[44-46]。但在乙腈的作用下,某些农药(如三氯杀螨醇等)易发生降解,通常可采用添加分析物保护剂的方式解决这个问题,如在乙腈中添加 0.1% 醋酸或者柠檬酸^[38,41]。此外,采用乙腈提取茶叶中的农药残留时,某些分析保护剂(如 5% 的氨水)不但可以提高农药回收率,还能降低茶叶中茶多酚、咖啡碱的影响,利于后续的净化操作^[47]。Amirahmadi 等^[40]则采用甲苯和乙醇(v:v=1:1)作为提取溶剂(极性和非极性溶剂的混合体系)提取红茶中的 25 种农药残留,以提高溶剂的穿透力,提升提取效果,同时解决了该方法后续采用 GCB 净化所引起的回收率较低的问题。

3.2.3 净化过程的优化

QuEChERS 方法的核心是寻求能够选择性吸附样品

提取溶液中干扰物质的净化剂,以达到净化样品的目的。目前使用较多的净化剂是 PSA,它能有效去除样品中的有机酸、极性色素、脂肪酸和糖。但和其他基质相比,茶叶除含有较多的生物碱、酚类物质和色素外,还含有蛋白质、氨基酸、果胶、有机酸和多糖等,其对净化剂的要求更高。因此,茶叶样品提取液通常需采用多种净化剂处理,以达到理想的净化效果。茶叶样品净化中常用的净化剂还有弗罗里硅土、 C_{18} 和 GCB 等。弗罗里硅土对蜡质等脂溶性杂质的去除效果明显;而 C_{18} 对非极性物质有较高的容量,对色素、甾醇和维生素的去除能力较强^[17]。GCB 对平面结构分子有很强的亲合性,能有效地去除固醇、叶绿素、咖啡碱和儿茶素等杂质^[44],但 GCB 同时对具有平面结构的农药有吸附作用,导致农药的回收率偏低,可在乙腈中加入一定比例的甲苯进行洗脱^[48]。叶江雷等^[35]在实验过程中采用 PSA、GCB、无水硫酸镁等净化,并对各种净化剂及用量进行优化选择,结果表明,当采用 PSA 和 GCB 复合净化剂净化提取液时,可有效去除样品溶液中的色素。张芬等^[49]分别考察了 PSA、GCB、氨基硅胶、SCX 离子交换填料、弗罗里硅土、 C_{18} 和硅胶等 7 种净化剂对干茶提取液中杂质的去除效果,结果表明,PSA、GCB 和弗罗里硅土复合净化剂对提取液的净化效果最好,且不影响农药的回收率。

随着研究的不断深入,许多新型净化剂应用于 QuEChERS 方法分析茶叶样品中的农药残留。Li 等^[50]采用氧化铁纳米颗粒和 GCB 混合物作为净化剂去除茶叶中的色素,不仅取得了良好的净化效果,也降低了分析费用。Hou 等^[39]人采用多壁碳纳米管和 PSA 净化茶叶的乙腈提取液,可同时分析茶叶中的 78 种农药残留,且在 0.05~0.15 mg/kg 的添加水平下,农药的回收率在 64.8%~116.3% 之间,相对标准偏差均小于 20%。Zhao 等^[43]在分析绿茶、乌龙茶和普洱茶中的 37 种农药残留时,采用多壁纳米管材料、PSA 和 GCB 吸附提取液中的干扰杂质。结果表明,在 10、20 $\mu\text{g}/\text{kg}$ 两个添加水平下,37 种农药的回收率为 70%~111%,相对标准偏差均小于 14%,检测限在 5~20 $\mu\text{g}/\text{kg}$ 之间。Deng 等^[51]以磁性纳米材料和多壁碳纳米管材料为净化剂替代传统的 GCB、PSA、 C_{18} 等填料净化茶叶的乙腈提取液,所得 8 种农药残留的回收率为 72.5%~109.1%,相对标准偏差均小于 12.6%。周利等^[52]采用可再生生物源材料纳米竹炭作为净化剂,分析绿茶中的灭多威等 10 种农药残留,结果显示,纳米竹炭作为净化剂在回收率、检出限及精密度等方面均能满足茶叶中农药残留分析的要求,且成本明显低于商品化基质分散吸附剂。由此可见,新型净化剂的开发和使用,可以提高样品的净化效果,降低检测成本。因此,开发新型的茶叶专用净化剂,如制备能特异性吸附茶叶中茶多酚、咖啡碱、茶氨酸、茶色素等成分的新型材料(如分子印迹聚合物或树脂材料等)可能成为未来的

研究方向之一。

4 结 语

和常规样品前处理技术相比,QuEChERS 方法较大幅度地解决了传统样品前处理技术所需时间长、有毒溶剂使用量大、共存物易干扰定性和定量等问题,尤其在多残留检测方面优势明显。然而值得注意的是,和其他食品基质相比,茶叶中的次生代谢产物多,基质效应明显,易对农药残留检测造成干扰;且各类标准对茶叶中农药残留的限量均较为严格。传统 QuEChERS 方法一般仅取 1 mL 上清液进行净化,这易造成净化后溶液中待分析农药的浓度较低,无法满足茶叶中农药残留低检测限量的要求;若增加上清液用量以提高浓缩倍数,则可能增加基质效应,影响检测的灵敏度。此外,QuEChERS 方法通常需结合价格昂贵的色谱-质谱联用仪进行检测,使得该方法难以推广普及。因此,开发茶叶专用的 QuEChERS 方法,提高检测灵敏度,降低对高精度检测仪器的要求是未来研究的重点,其中开发新型的茶叶专用净化剂可能是其关键。此外,随着色谱-质谱联用仪等精密仪器的快速发展和成本的不断降低,QuEChERS 方法与这些检测仪器联用将更加成熟,使得该技术应用于茶叶日常农药多残留的监测及标准方法成为可能。

参考文献

- [1] 中华合作时报. 农业部发布 2013 年中国茶叶种植生产情况. <http://www.chajie.com/Article-12060.html>. 2014-08-06.
China co-operation times. The tea planting and growing in China in 2013 issued by Ministry of Agriculture of the People's Republic of China. <http://www.chajie.com/Article-12060.html>. 2014-08-06.
- [2] 中国茶叶网. 2013 年 12 月世界主要产茶国家和地区茶叶产量. <http://www.e-chinatea.cn/market/info/28278.aspx>. 2014-08-06.
Web of China tea. The tea production of the world's major countries and regions in December 2013. <http://www.e-chinatea.cn/market/info/28278.aspx>. 2014-08-06.
- [3] 中华合作时报. 2013 年全球茶叶贸易持续增加. http://www.zh-hz.com/dz/html/2014-05/27/content_92326.htm. 2014-08-06.
China co-operation times. Global tea trade increase in 2013. http://www.zh-hz.com/dz/html/2014-05/27/content_92326.htm. 2014-08-06.
- [4] 中华人民共和国商务部. 中国茶叶遭遇农药残留壁垒概述. <http://policy.mofcom.gov.cn/export/tea2014/c3.action#b32>. 2014-08-03.
Ministry of Commerce of the People's Republic of China. Chinese tea encounters pesticide residue barriers. <http://policy.mofcom.gov.cn/export/tea2014/c3.action#b32>. 2014-08-03.
- [5] 胡贝贞, 宋伟华, 谢丽萍, 等. 加速溶剂萃取/凝胶渗透色谱-固相萃取净化/气相色谱-质谱法测定茶叶中残留的 33 种农药[J]. 色谱, 2008, 26(1): 22-28.
Hu BZ, Song WH, Xie LP, *et al.* Determination of 33 pesticides in tea using accelerated solvent extraction/gel permeation chromatography and solid phase extraction/gas chromatography-mass spectrometry [J]. *Chin J Chromatogr*, 2008, 26(1): 22-28.

- [6] Cai L, Xing J, Dong L, *et al.* Application of polyphenylmethylsiloxane coated fiber for solid-phase microextraction combined with microwave-assisted extraction for the determination of organochlorine pesticides in chinese teas [J]. *J Chromatogr A*, 2003, 1015(1-2): 11–21.
- [7] Huang SP, Huang SD. Dynamic hollow fiber protected liquid phase microextraction and quantification using gas chromatography combined with electron capture detection of organochlorine pesticides in green tea leaves and ready-to-drink tea [J]. *J Chromatogr A*, 2006, 1135(1): 6–11.
- [8] 侯英, 曹秋娥, 谢小光, 等. 应用搅拌棒吸附萃取-热脱附-气相色谱-质谱测定烟叶和茶叶中拟除虫菊酯类农药残留 [J]. *色谱*, 2007, 25(1): 25–29.
- Hou Y, Cao QE, Xie XG, *et al.* Determination of pyrethroid pesticide residues in tobacco leaves and tea using stir bar sorptive extraction-thermal desorption and gas chromatography-mass spectrometry [J]. *Chin J Chromatogr*, 2007, 25(1): 25–29.
- [9] Li B, Zeng F, Dong Q, *et al.* Rapid determination method for 12 pyrethroid pesticide residues in tea by stir bar sorptive extraction-thermal desorption-gas chromatography [J]. *Physics Procedia*, 2012, 25: 1776–1780.
- [10] Ji J, Deng C, Zhang H, *et al.* Microwave-assisted steam distillation for the determination of organochlorine pesticides and pyrethroids in chinese teas [J]. *Talanta*, 2007, 71(3): 1068–1074.
- [11] Hu YY, Zheng P, He YZ, *et al.* Response surface optimization for determination of pesticide multiresidues by matrix solid-phase dispersion and gas chromatography [J]. *J Chromatogr A*, 2005, 1098(1-2): 188–193.
- [12] 易江华, 段振娟, 方国臻, 等. QuEChERS 方法在食品农药残留检测中的应用 [J]. *中国食品学报*, 2013, 13(2): 153–158.
- Yi JH, Duan ZJ, Fang GZ, *et al.* Study of QuEChERS method for the detection of pesticide and veterinary drug residues in foods [J]. *J Chin Inst Food Sci Technol*, 2013, 13(2): 153–158.
- [13] Anastassiades M, Lehotay SJ, Stajnbaher D, *et al.* Fast and easy multiresidue method employing acetonitrile extraction/partitioning and "dispersive solid-phase extraction" for the determination of pesticide residues in produce [J]. *J AOAC Int*, 2003, 86(2): 412–431.
- [14] Lehotay SJ, Mastovska K, Lightfield AR. Use of buffering and other means to improve results of problematic pesticides in a fast and easy method for residue analysis of fruits and vegetables [J]. *J AOAC Int*, 2005, 88(2): 615–629.
- [15] Lehotay SJ, De Kok A, Hiemstra M, *et al.* Validation of a fast and easy method for the determination of residues from 229 pesticides in fruits and vegetables using gas and liquid chromatography and mass spectrometric detection [J]. *J AOAC Int*, 2005, 88(2): 595–614.
- [16] Anastassiades M, Scherbaum E, Tasdelen B, *et al.* Recent developments in QuEChERS methodology for pesticide multiresidue analysis, in *Pesticide chemistry* [B]. Wiley-VCH Verlag GmbH & Co. KGaA, 2007, 439–458.
- [17] Wilkowska A, Biziuk M. Determination of pesticide residues in food matrices using the QuEChERS methodology [J]. *Food Chem*, 2011, 125(3): 803–812.
- [18] Sobhanzadeh E, Abu Bakar NK, Bin Abas MR, *et al.* A simple and efficient multi-residue method based on QuEChERS for pesticides determination in palm oil by liquid chromatography time-of-flight mass spectrometry [J]. *Environ Monit Assess*, 2012, 184(9): 5821–5828.
- [19] Nguyen TD, Lee BS, Lee BR, *et al.* A multiresidue method for the determination of 109 pesticides in rice using the quick easy cheap effective rugged and safe QuEChERS sample preparation method and gas chromatography/mass spectrometry with temperature control and vacuum concentration [J]. *Rapid Commun Mass Spectrom*, 2007, 21(18): 3115–3122.
- [20] Mantzos N, Karakitsou A, Zioris I, *et al.* QuEChERS and solid phase extraction methods for the determination of energy crop pesticides in soil, plant and runoff water matrices [J]. *Int J Environ Anal Chem*, 2013, 93(15): 1566–1584.
- [21] Chen L, Song F, Liu Z, *et al.* Multi-residue method for fast determination of pesticide residues in plants used in traditional chinese medicine by ultra-high-performance liquid chromatography coupled to tandem mass spectrometry [J]. *J Chromatogr A*, 2012, 1225: 132–140.
- [22] Surma M, Sadowska-Rociek A, Cieřlik E. Evaluation of the QuEChERS method with gc-ms detection for the determination of organochlorine pesticides in food of animal origin [J]. *Food Anal Method*, 2014, 7(2): 366–376.
- [23] Karageorgou EG, Samanidou VF. Development and validation according to european union decision 2002/657/ec of an hplc-dad method for milk multi-residue analysis of penicillins and amphenicols based on dispersive extraction by QuEChERS in mspd format [J]. *J Sep Sci*, 2011, 34(15): 1893–1901.
- [24] Freitas S, Paim A, De Souza e Silva P. Development of a lc-it-tof ms procedure to quantify veterinary drug residues in milk employing a QuEChERS approach [J]. *Food Anal Method*, 2014, 7(1): 39–46.
- [25] Garrido Frenich A, Aguilera-Luiz Mdel M, Martinez Vidal JL, *et al.* Comparison of several extraction techniques for multiclass analysis of veterinary drugs in eggs using ultra-high pressure liquid chromatography-tandem mass spectrometry [J]. *Anal Chim Acta*, 2010, 661(2): 150–160.
- [26] Wiest L, Buleté A, Giroud B, *et al.* Multi-residue analysis of 80 environmental contaminants in honeys, honeybees and pollens by one extraction procedure followed by liquid and gas chromatography coupled with mass spectrometric detection [J]. *J Chromatogr A*, 2011, 1218(34): 5743–5756.
- [27] Wozniak B, Zuchowska IM, Zmudzki J. Determination of stilbenes and resorcylic acid lactones in bovine, porcine and poultry muscle tissue by liquid chromatography-negative ion electrospray mass spectrometry and QuEChERS for sample preparation [J]. *J Chromatogr B*, 2013, 940: 15–23.
- [28] Jia W, Ling Y, Lin Y, *et al.* Analysis of additives in dairy products by liquid chromatography coupled to quadrupole-orbitrap mass spectrometry [J]. *J Chromatogr A*, 2014, 1336: 67–75.
- [29] Pincemaille J, Schummer C, Heinen E, *et al.* Determination of polycyclic aromatic hydrocarbons in smoked and non-smoked black teas and tea infusions [J]. *Food Chem*, 2014, 145: 807–813.
- [30] 韩深, 王珮玥, 刘莹, 等. QuEChERS 净化技术结合超高效液相色谱-串联质谱法筛查食用贝类中的 3 种原甲藻类毒素 [J]. *色谱*, 2013, 31(10): 939–945.
- Han S, Wang PY, Liu Y, *et al.* Determination of three azaspiracids in edible shellfishes by QuEChERS method combined with ultra high performance liquid chromatography-tandem mass spectrometry [J]. *Chin J Chromatogr*, 2013, 31(10): 939–945.
- [31] Vaclavik L, Zachariasova M, Hrbek V, *et al.* Analysis of multiple mycotoxins in cereals under ambient conditions using direct analysis in real time (dart) ionization coupled to high resolution mass spectrometry [J]. *Talanta*, 2010, 82(5): 1950–1957.
- [32] Usui K, Hayashizaki Y, Hashiyada M, *et al.* Rapid drug extraction from human whole blood using a modified QuEChERS extraction method [J].

- Leg Med (Tokyo), 2012, 14(6): 286–296.
- [33] Klinsunthorn N, Petsom A, Nhujak T. Determination of steroids adulterated in liquid herbal medicines using QuEChERS sample preparation and high-performance liquid chromatography [J]. J Pharm Biomed Anal, 2011, 55(5): 1175–1178.
- [34] 黄诚, 郭梅, 张怀宇, 等. 茶叶中 8 种拟除虫菊酯类农药残留 QuEChERS-气相色谱检测法 [J]. 职业与健康, 2012, 28(1): 43–45.
Huang C, Guo M, Zhang HY, *et al.* Determination of 8 pyrethroid pesticide residues in tea by QuEChERS-Gas Chromatography [J]. Occup Health, 2012, 28(1): 43–45.
- [35] 叶江雷, 金贵娥, 吴云辉, 等. QuEChERS 法提取净化结合气-质联法快速检测茶叶中农药残留 [J]. 食品科学, 2013, 34(12): 265–271.
Ye J, Jin GE, Wu YH, *et al.* Rapid determination of pesticide residues in tea by QuEChERS and gas chromatography-mass spectrometry (GC-MS) [J]. Food Sci, 2013, 34(12): 265–271.
- [36] Lozano A, Rajski L, Belmonte-Valles N, *et al.* Pesticide analysis in teas and chamomile by liquid chromatography and gas chromatography tandem mass spectrometry using a modified QuEChERS method: Validation and pilot survey in real samples [J]. J Chromatogr A, 2012, 1268: 109–122.
- [37] Zhang Y, Xu H. Determination of triazoles in tea samples using dispersive solid phase extraction combined with dispersive liquid-liquid microextraction followed by liquid chromatography-tandem mass spectrometry [J]. Food Anal Method, 2014, 7(1): 189–196.
- [38] Chen G, Cao P, Liu R. A multi-residue method for fast determination of pesticides in tea by ultra performance liquid chromatography-electrospray tandem mass spectrometry combined with modified QuEChERS sample preparation procedure [J]. Food Chem, 2011, 125(4): 1406–1411.
- [39] Hou X, Lei S, Qiu S, *et al.* A multi-residue method for the determination of pesticides in tea using multi-walled carbon nanotubes as a dispersive solid phase extraction absorbent [J]. Food Chem, 2014, 153: 121–129.
- [40] Amirahmadi M, Shoeibi S, Abdollahi M, *et al.* Monitoring of some pesticides residue in consumed tea in tehran market [J]. Iranian J Environ Health Sci Eng, 2013, 10(1): 9.
- [41] Cajka T, Sandy C, Bachanova V, *et al.* Streamlining sample preparation and gas chromatography-tandem mass spectrometry analysis of multiple pesticide residues in tea [J]. Anal Chim Acta, 2012, 743: 51–60.
- [42] 贾玮, 黄峻榕, 凌云, 等. 高效液相色谱-串联质谱法同时测定茶叶中 290 种农药残留组分 [J]. 分析测试学报, 2013, 32(1): 9–22.
Jia W, Huang JR, Ling Y, *et al.* Determination of 290 pesticide residues in tea by high performance liquid chromatography-tandem mass spectrometry [J]. J Instrum Anal, 2013, 32(1): 9–22.
- [43] Zhao P, Wang L, Jiang Y, *et al.* Dispersive cleanup of acetonitrile extracts of tea samples by mixed multiwalled carbon nanotubes, primary secondary amine, and graphitized carbon black sorbents [J]. J Agric Food Chem, 2012, 60(16): 4026–4033.
- [44] 张新忠, 罗逢健, 陈宗懋, 等. 超高效液相色谱-四极杆飞行时间质谱测定茶叶中手性农药茚虫威对映体残留 [J]. 质谱学报, 2012, 33(6): 321–326.
Zhang, XZ, Luo FJ, Chen ZM, *et al.* Enantioseparation and quantification of chiral pesticide indoxacarb residues in tea by UHPLC-O-TOF/MS [J]. J Chin Mass Spectrom Soc, 2012, 33(6): 321–326.
- [45] Li Y, Chen X, Fan C, *et al.* Compensation for matrix effects in the gas chromatography-mass spectrometry analysis of 186 pesticides in tea matrices using analyte protectants [J]. J Chromatogr A, 2012, 1266: 131–142.
- [46] Payá P, Anastassiades M, Mack D, *et al.* Analysis of pesticide residues using the quick easy cheap effective rugged and safe (QuEChERS) pesticide multiresidue method in combination with gas and liquid chromatography and tandem mass spectrometric detection [J]. Anal Bioanal Chem, 2007, 389(6): 1697–1714.
- [47] 张新忠, 罗逢健, 陈宗懋, 等. 分散固相萃取净化超高效液相色谱串联质谱法研究茶叶与茶汤中茚虫威残留降解规律 [J]. 分析测试学报, 2013, 32(1): 1–8.
Zhang XZ, Luo FJ, Chen ZM, *et al.* Study of indoxacarb residue degradation in tea and tea infusion by ultra high performance liquid chromatography coupled with tandem mass spectrometry after dispersive solid phase extraction cleanup [J]. J Instrum Anal, 2013, 32(1): 1–8.
- [48] Zhao L, Stevens J. Optimizing recoveries of planar pesticides in spinach using toluene and agilent bond elut aoac QuEChERS kits with graphitized carbon. Available from: <https://www.chem.agilent.com/Library/applications/5990-4247EN.pdf>. 2014-08-01.
- [49] 张芬, 张新忠, 罗逢健, 等. QuEChERS 净化 GC/ECD 测定茶叶与土壤中噻虫嗪、虫螨腈及高效氯氟氰菊酯残留 [J]. 分析测试学报, 2013, 32(4): 393–400.
Zhang F, Zhang XZ, Luo FJ, *et al.* Residue analysis of thiamethoxam, chlorfenapyr and lambda-cyhalothrin in tea and soil by GC/ECD after QuEChERS clean-up [J]. J Instrum Anal, 2013, 32(4): 393–400.
- [50] 李媛, 肖光辉, 周乃元, 等. 在茶叶农药残留测定中用四氧化三铁纳米粒子去除样品中的色素 [J]. 分析化学, 2013, 41(1): 63–68.
Li Y, Xiao LH, Zhou NY, *et al.* Purification of pigments by iron oxide nanoparticles for analysis of pesticide residues in tea [J]. Chin J Anal Chem, 2013, 41(1): 63–68.
- [51] Deng X, Guo Q, Chen X, *et al.* Rapid and effective sample clean-up based on magnetic multiwalled carbon nanotubes for the determination of pesticide residues in tea by gas chromatography-mass spectrometry [J]. Food Chem, 2014, 145: 853–858.
- [52] 周利, 罗逢健, 张新忠, 等. 纳米竹炭分散固相萃取/超高效液相色谱-串联质谱法测定绿茶中的农药多残留 [J]. 分析测试学报, 2014, 33(6): 642–647.
Zhou L, Luo FJ, Zhang XZ, *et al.* Determination of multi-pesticide residues in green tea by nano bamboo charcoal-dSPE/ultra high performance liquid chromatography-tandem mass spectrometry [J]. J Instrum Anal, 2014, 33(6): 642–647.

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