QuEChERS

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摘　要: QuEChERS 法是一种用于检测蔬菜水果中农药多残留的前处理方法，因其简单高效而得到广泛的应用。随着面对的基质越来越复杂，QuEChERS 法也在不断地进行优化改良。因此研究人员会根据基质的不同性质，在提取溶剂、缓冲盐、盐析、净化材料等方面不断的进行优化，得到更好的实验效果。本研究在阐述传统 QuEChERS 法的基础上，从方法的关键步骤，提取和净化 2 方面进行分析，系统阐述了近几年 QuEChERS 法的改良过程及其在农药多残留检测方面的应用，为 QuEChERS 法在不同类型基质的检测应用提供参考。

关键词: 改良 QuEChERS 法；农药多残留；样品前处理

Application of the modified QuEChERS in the multi-class pesticide residues

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ABSTRACT: QuEChERS method is a pretreatment method for detecting pesticide residues in fruits and vegetables. It is widely used because of its simplicity and high efficiency. As the matrix is becoming more and more complex, the QuEChERS method is constantly improving. Therefore, according to the different properties of the substrate, researchers will continuously optimize the extraction solvent, buffer salt, salting out, purification material and other aspects to get better experimental results. Based on the traditional QuEChERS method, this study analyzed the key steps, extraction and purification of the method, and systematically expounded the improvement process of QuEChERS method in recent years and its application in pesticide multi-residue detection, so as to provide reference for QuEChERS method to detect applications of different types of substrates.

KEY WORDS: modified QuEChERS; multi-class pesticide residues; sample pretreatment

1　引　言

我国是一个传统农业大国，农业种植业大多以分散种植为主，一些种植户会为了提高农作物产量而盲目的使用农药，这不仅容易造成农产品农药残留超标、农业生态环境受到污染和破坏的严重后果，而且会对人的身体健康造成不良影响。因此，建立准确快速的农药残留检测方法对于监控农产品和环境中的农药残留具有重要作用。目前，农药残留检测确证方法主要依托仪器分析方法，如色谱、色谱串联质谱等技术，而仪器检测必须先对样品进行复杂的前处理。当前农药残留检测中常见的样品前处理方法有固相萃取(solid-phase extraction, SPE)[1,2]、固相微萃取(solid-phase microextraction, SPME)[3]、超临界流体萃取(supercritical fluidextraction, SFE)[4]、分散液液微萃取(dispersive

liquid-liquid microextraction, DLLME)[5-7]、加速溶剂萃取 (accelerated solvent extraction, ASE)[8,9]、凝胶渗透色谱(gel permeation chromatography, GPC)[10-12]、基质分散固相萃取 (matrix solid-phase dispersion, MSPD)[13-15]、QuEChERS (quick, easy, cheap, effective, rugged, safe) 法[16-18] 等。QuEChERS 法是一种针对蔬菜水果中农药多残留检测的方法，由美国学者 Anastassiades 等[19]于 2003 年首次提出，因其处理效果远高于其他前处理方法而得到全世界各检验机构的认可，目前已广泛应用于农药残留检测中。

本文在介绍传统 QuEChERS 法的基础上，结合近些年不同类型样品的前处理技术研究现状，从提取和净化 2 个方面简要阐述了改良 QuEChERS 方法在农药多残留检测方面的研究和应用，为 QuEChERS 法在不同类型基质的检测方面提供参考。

2　传统 QuEChERS 法

QuEChERS 法[19]具体的步骤如下：称取 10 g 样品于 50 mL 离心管中，加入 10 mL 乙腈、4 g 无水硫酸镁、1 g 氯化钠，振摇离心，取上清液于装有无水硫酸镁(质量浓度为 150 mg/mL)和 N-丙基乙二胺(primary secondary amine, PSA) (质量浓度为 25 mg/mL)的 15 mL 离心管中，振摇离心，取上清液过膜上机。可根据实际情况按比例增减取样量和提取溶剂量，可根据样品中脂肪酸和叶绿素等干扰物的含量来选择性的添加石墨化碳黑(Graphitized Carbon Black, GCB) (质量浓度为 50 mg/mL)和八甲基硅烷 (octadecyl silane, C$_{18}$) (质量浓度为 50 mg/mL)。

QuEChERS 法主要包括 2 个关键步骤：(1) 提取，向样品中添加乙腈提取待测目标组分，并加入盐来减少待测目标组分在水中的残留；(2) 净化，采用分散固相萃取的原理，利用吸附剂除去待测目标组分中的干扰物质。

在提取方面，研究人员考察了乙腈、丙酮和乙酸乙酯这 3 种提取溶剂之后选择了乙腈。主要原因是尽管乙腈有较大的膨胀系数、低挥发性、高毒性、不利于氮磷检测器和电子捕获检测器等缺点，但是它的优点也非常明显：针对不同极性范围的残留农药都具有很好的提取效果；能与水混溶，在盐的作用下又能与水两相分离；提取出较少的亲脂性干扰物等。增加氯化钠有利于有机相与水相的分离，同时有利于提高大极性目标化合物的回收率。添加无水硫酸镁可以吸收水，促进待测物在有机相的分配，同时无水硫酸镁吸水放出的热量有利于非极性目标化合物的提取。

在净化过程中使用的吸附剂主要有 PSA、GCB 和 C$_{18}$，其中 PSA 主要去除糖类、有机酸等极性化合物，GCB 主要去除叶绿素、类胡萝卜素等色素，C$_{18}$ 主要去除脂肪酸和固醇类化合物。根据不同样品的基质特点来单独或组合使用这 3 种吸附剂，从而达到净化的目的。

QuEChERS 法后来衍生出 AOAC[20]和 CEN[21]2 种版本，AOAC 以 1%的酸化乙腈为提取溶剂，提取过程加入乙酸钠为缓冲盐，CEN 则以柠檬酸钠和柠檬酸二钠为缓冲盐。缓冲盐的加入有利于提高对 pH 敏感的农药残留(如吡蚜酮、噻菌灵等)的回收率。

QuEChERS 法体现出极强的灵活性，可以同时提取性质不同、极性差异很大的目标化合物，在农药[22,23]、兽药[24,25]、环境残留物[26-28]、生物毒素[29,30]、制药[31,32]等检测方面广泛应用。同时，除了蔬菜水果以外，其对谷物[33,34]、油料[15,35]、乳制品[36,37]、土壤[38,39]、茶叶[8,40]、蜂蜜[41,42]、烟草[13]等多种基质也有很好的净化效果。

3　改良 QuEChERS 法及其在农药多残留检测方面的应用

QuEChERS 法的提出为农药多残留的检测提供了方便，但研究人员也发现有一些农药残留(如百菌清、吡蚜酮等)并不适用传统 QuEChERS 法。针对具体的基质和农药残留项目，对 QuEChERS 法进行优化之后，可以得到更好的实验结果。因此，研究人员在提取和净化这两个主要的步骤中改良，使其更加适合于目标化合物的检测。

3.1　优化提取过程的 QuEChERS 法及其应用

提取过程是使用提取溶剂通过液—液、液—固等方式萃取出基质中的待测目标物，同时用盐使有机相与水相分离。根据不同特性的基质和待测农药来选择不同的溶剂及盐以达到最佳的提取效果。其优化主要有 2 个方面：(1) 提取溶剂，(2) 缓冲盐及盐析过程。

3.1.1　提取溶剂的选择和应用

提取溶剂既要满足对目标化合物有尽可能好的提取效果，减少其降解损失，又要能尽量少地提取出基质中的干扰物。因此，在面对复杂的样品基质时，研究人员使用了不同的提取溶剂得到更好的提取效果。Stöckelhuber 等[43]在研究农药残留对土壤的影响时，采用气相色谱串联质谱法测定了 9 种常用于葡萄的农药在葡萄藤下土壤中节肢动物和腹足动物体内的残留情况。对比了乙腈和乙酸乙酯的提取效果，发现乙腈提取物的峰面积比乙酸乙酯的要小的多，考虑到乙腈的毒性，选择乙酸乙酯作为提取溶剂，加上 PSA 和无水硫酸镁的净化，得到 9 种农残的加标回收率为 84%~110%，相对标准偏差小于 18%，检出限为 0.02~0.20 mg/kg(质量分数)。Li 等[44]研究果蔬中 5 种农药残留时，使用 Plackett-Burman 试验筛选并用 central composite design (CCD)优化，得到结果为使用乙腈:甲苯 =1:1 (V:V)加入 0.25%盐酸有最佳的提取效果，加入盐酸是因为 2,4-D 具有较强的酸性，降低 pH 有利于其稳定性；加入甲苯则是为了提高多菌灵、异菌脲等农药的回收率。Maestroni 等[45]使用气相色谱串联质谱法测定葡萄叶中 59 种农药残留时，用酸化乙酸乙酯作为提取溶剂，对中小极

性农药项目有很好的提取效果，同时能大幅度减少基质中干扰物的共提取。但是，这种提取溶剂对极性较大的物质回收率会很低，不适用于大极性农药残留的测定。

3.1.2 缓冲盐及盐析过程的选择和应用

缓冲盐能保证对 pH 敏感的待测目标组分的稳定，盐析的作用是促进有机相与水相的分离，促进待测物在有机相中的分配。Faraji 等[46]在检测无花果中啶虫脒、吡虫啉、螺虫乙酯及其代谢残留时发现使用带有碳酸氢钠的盐包的提取效果最好。碳酸氢钠的存在对螺虫乙酯及其代谢物的回收率影响不大，但是却能明显提高啶虫脒、吡虫啉及其代谢产物的回收率，这是因为啶虫脒、吡虫啉及其代谢产物为碱性化合物，碳酸氢钠能减少它们的离子化。

3.2 优化净化过程的 QuEChERS 法及其应用

PSA、GCB、C_{18} 等吸附剂都有各自的优缺点: PSA 因为含有 2 个胺基而带碱性，对灭菌丹、抑菌灵等酸性农药的回收率会有影响[47]，GCB 会吸附具有平面结构的化合物，降低六氯苯、噻菌灵等农药的回收率[48]，C_{18} 则会吸附一些农药如噻嗪酮、戊唑醇，降低其回收率[49]。为改善这些易受影响农药的回收率，研究人员试验这 3 种吸附剂不同比例的组合，也尝试了各种不同的材料，并取得了令人满意的效果。净化方面的优化包括根据不同的基质调整 PSA、GCB、C_{18} 等吸附剂的含量和使用其他吸附材料来净化基质。

3.2.1 调整吸附剂的成分含量和其他实验条件

研究人员利用统计软件从理论角度考察溶剂体积、缓冲盐、各种吸附剂的含量等影响因素，得出对结果有较大关联的变量，再用优化软件来拟合得到一条曲线，计算出最优方案。Manav 等[36]利用 Plackett-Burman experimental design (PBD)来筛选乙腈体积、甲酸含量、氯化钠、无水硫酸钠、乙酸钠、硅藻土、无水硫酸镁、C_{18} 的质量等变量，再用 Box-Behnken design (BBD)方法优化确定提取净化效果的最佳组合。结果显示，测定乳制品中 25 种农残含量时取样量为 10 g，添加 10 mL 乙腈(含 1%的甲酸)，使用 5.7 g 氯化钠、6 g 无水硫酸钠、4.2 g 乙酸钠提取，振荡离心后，取 7 mL 上清液用 0.5 g 硅藻土、300 mg 无水硫酸镁、150 mg C_{18} 净化，使用气质联用检测得到满意结果。Viera 等[50]利用全因子设计(full factorial design)筛选得到: 3 g 样品用 10 mL 含 5%的甲酸乙腈提取，用 1.5 g 氯化钠、4 g 无水硫酸镁分离，振荡离心后取 2 mL 上清液用 300 mg 无水硫酸镁、50 mg C_{18}、10 mg GCB 净化可以得到较好的效果，能满足欧盟文件 SANTE/11945/2015[51]的要求。Li 等[52]同样利用 PBD 和 CCD 来优化吸附剂的含量，得到回收率 71%~119.5%，相对标准偏差小于 12.1%的结果。

另外，也有研究通过比较不同的吸附剂组分和含量的加标回收实验来确定最优的吸附剂的添加量。Qin 等[53]利用液相色谱串联质谱法测定了苹果、花生、小麦、茶叶等不同基质中 23 种农药多残留含量，针对不同基质采用

了不同的吸附剂，取得了良好的效果。对于苹果等高水分基质，使用 5 mg 富氮活性炭(nitrogen-enriched activated carbon)、30 mg PSA、150 mg 无水硫酸镁；对于花生、小麦等含高油高淀粉的基质，使用 5 mg 富氮活性炭、30 mg C_{18}、150 mg 无水硫酸镁；对于茶叶等复杂基质，使用 15 mg 富氮活性炭、20 mg GCB、150 mg 无水硫酸镁。Huang 等[54]使用液相色谱串联质谱法测定绿茶中农药多残留时，增加 GCB 和 C_{18} 的含量以应对茶叶中的复杂干扰物。Zhan 等[55]在测定不同种类的果蔬中的农药多残留时采用不同种类的吸附剂，用 GCB 去净化小白菜等含叶绿素丰富的基质，用 C_{18} 去净化葡萄等含糖高的基质，对西瓜等干扰较少的基质则只用无水硫酸镁除水。Da-Costa-Morail 等[56]在使用液相色谱串联质谱法测定甜椒中农药多残留时发现，使用 PSA 和无水硫酸镁无法完全除去乙腈提取物中的干扰，于是增加了 GCB 来提高净化效果。

3.2.2 使用新型材料作为吸附剂

净化过程在 QuEChERS 法起到非常关键的作用，因此大量研究者在不断探索新型材料作为吸附剂，有研究报道的材料有 Z-Sep[37,41,57-59]、壳聚糖[38]、磁性纳米粒子 (magnetic nanoparticles, MNPs)[60]、石墨烯氧化物 tri-BuA-rGO[61]、氟化吸附剂[62]、酚醛基活性碳纤维 (phenolic resin based activated carbon fibers, ACFs)[63]等，这些材料作为净化过程的吸附剂取得了良好的效果。

Rejczak 等[37]使用液相色谱联用二极管阵列检测器测定牛乳中 30 种农药残留含量，净化过程采用 PSA 去除脂肪酸、糖类及极性脂类，Z-Sep 和 Z-Sep Plus 去除非极性脂类，大多数结果能满足欧盟文件 SANTE/11945/2015[51]的要求。用此方法筛查了市售的部分牛乳样品，发现 7 种农药残留，质量浓度为 0.3~18.7 ng/mL。在取得同等净化效果的情况下，该方法中 Z-Sep 和 Z-Sep Plus 比其他吸附剂更加廉价，也适用于二极管阵列检测器，而不必用昂贵的质谱仪。Moreno-González 等[58]测定各类食用油中的农药多残留，在使用乙腈作为提取溶剂的情况下，对比了 Z-Sep Plus、C_{18}+PSA 组合的净化效果，发现前者能显著降低基质效应，也就是说 Z-Sep Plus 去除脂类的效果较 C_{18} 和 PSA 更好。Salles 等[64]测定咖啡叶中 52 种农药多残留时发现咖啡因和农药残留在被 PSA、C_{18} 等吸附剂吸附时会存在竞争关系，在使用 PSA、C_{18} 等吸附剂时，咖啡因的含量远高于添加在空白样中的农药残留，然而加入 Z-Sep Plus 后，咖啡因的含量有明显的减少。测试结果表明 PSA、C_{18} 净化时基质效应高达 97%，添加 Z-Sep Plus 后基质效应下降至 32%，同时回收率得到了很大的改善。对于蜜蜂[41]、啤酒花[59]、头发[57]等其他基质的农药多残留的测定，Z-Sep 和 Z-Sep Plus 或单独使用，或连同其他吸附剂一起使用，都表现出较好的吸附效果。

Dd-Oliveira-Arias 等[38]测定稻田土壤中 17 种农药残

留含量时发现, 在不净化的情况下得到的结果勉强满意: 回收率为 54%~141%, 相对标准偏差小于 21%; 但是, 其中有 8 种化合物的基质效应大于 20%。因此, 实验考察了 PSA、硅藻土、几丁质、壳聚糖等 4 种吸附剂的净化效果, 结果发现: PSA 适用于净化酸性物质, 但稻田使用的农药大部分是酸性, 会影响回收率; 硅藻土的净化效果不如几丁质、壳聚糖, 而壳聚糖更加常见; 最终, 实验选择壳聚糖作为吸附剂去净化基质。Fernandes 等[60]把自制的 MNPs 用于草莓的 7 种有机磷的检测中, 从测试谱图可以看出添加磁性纳米微粒可以更加充分的去除基质中的糖、有机酸、色素等干扰物, 得到更加干净的谱图。同时, 该研究对几种磁性纳米微粒与常用吸附剂的搭配、吸附剂的含量、净化的时间等方面进行了优化, 得出的结论是使用 10 mg Fe_3O_4@TEOS@MPS MNPs 和 10 mg PSA, 振荡 30 s 时的净化效果最佳。Ma 等[61]合成了不同长度碳链的氨基石墨烯氧化物, 利用其物理性质来吸附茶叶中的儿茶素、咖啡因、色素等干扰物, 从而达到净化的效果。实验表明, tri-BuA-rGO 对儿茶素、咖啡因的吸附效果最好也能除去大量的色素, 同时其吸附能力也远大于 PSA、C_{18}、GCB 等吸附剂, 有成为新的吸附剂的潜力。Martins 等[62]通过在硅胶表面固定含氟聚合物得到 1 种氟化吸附剂, 在测定番茄甜椒的农药多残留时体现出比传统吸附剂更好的净化效果, 也提高了待测物的回收率。Singh 等[63]使用 ACFs 净化多种农产品中的 26 种农药残留, 对比实验发现 ACFs 比 PSA 有更好的净化效果和回收率表现。

　　由此可见, 新材料的筛选和使用在得到更好的实验效果的同时, 也丰富了 QuEChERS 法吸附材料的储备库, 为其使用范围的扩大提供了基础, 使其能够拥有更广阔的应用空间。

4 展　望

　　QuEChERS 法自 2003 年问世以来, 在短短几年的时间内得到了迅速的发展, 世界各地的检测机构都采用该方法进行农药多残留检测的样品前处理, 极大地提高了检测效率, 提高了不同基质样品检测结果的准确性和稳定性, 使得农药多残留样品前处理技术具备了简便、快速、高效、准确等特点。

　　但是, 目前该方法依然是以人工操作为主, 后一阶段的发展趋势应该是在保证实验结果准确的前提下, 减少实验所需样品含量, 提高单批次样品的处理量, 并实现提取和净化过程自动化, 更进一步的减轻检测人员的负担, 提高工作效率。同时, 由于当前市面流通的农药种类有上千种, 而且新型低毒高效农药、复合农药不断诞生, 常规的农药多残留检测技术已经无法满足要求。随着高分辨质谱的发展, 利用质谱数据库, 可以实现无需依赖标准品而对农药多残留进行快速、准确、高通量的筛查分析。

QuEChERS 法可利用其简单快速的前处理技术与高分辨质谱强强联合, 提高筛查效率。相信 QuEChERS 法将会通过不断的调整和改良来应对更为复杂的基质, 各种新的改良 QuEChERS 法也必然会为检测工作提供更大的便利, 在食品、生物样品、环境监测、医药等方面会拥有更加广阔的应用前景。

参考文献

[1] Liu GY, Li LY, Huang XD, *et al*. Determination of triazole pesticides in aqueous solution based on magnetic graphene oxide functionalized MOF-199 as solid phase extraction sorbents [J]. Micropor Mesopor Mat, 2018, 270: 258–264.

[2] Salemi A, Khaleghifar N, Mirikaram N. Optimization and comparison of membrane-protected micro-solid-phase extraction coupled with dispersive liquid-liquid microextraction for organochlorine pesticides using three different sorbents [J]. Microchem J, 2019, 144: 215–220.

[3] Al-Alam J, Fajloun Z, Chbani A, *et al*. A multiresidue method for the analysis of 90 pesticides, 16 PAHs, and 22 PCBs in honey using QuEChERS–SPME [J]. Anal Bioanal Chem, 2017, 409(21): 5157–5169.

[4] King JW, Johnson JH, Taylor SL, *et al*. Simultaneous multi-sample supercritical-fluid extraction of food products for lipids and pesticide residue analysis [J]. J Super-Crit Fluids, 1995, 8(2): 167–175.

[5] Bresin B, Piol M, Fabbro D, *et al*. Analysis of organo-chlorine pesticides residue in raw coffee with a modified "quick easy cheap effective rugged and safe" extraction/clean up procedure for reducing the impact of caffeine on the gas chromatography-mass spectrometry measurement [J]. J Chromatogr A, 2015, 1376: 167–171.

[6] Li JX, Sun MY, Chang QY, *et al*. Determination of pesticide residues in teas via QuEChERS combined with dispersive liquid–liquid microextraction followed by gas chromatography–tandem mass spectrometry [J]. Chromatographia, 2017, 80(9): 1447–1458.

[7] Lawal A, Wong RCS, Tan GH, *et al*. Multi-pesticide residues determination in samples of fruits and vegetables using chemometrics approach to QuEChERS-dSPE coupled with ionic liquid-based DLLME and LC–MS/MS [J]. Chromatographia, 2018, 81(5): 759–768.

[8] Abdul-Kadir H, Abasb F, Mediani A, *et al*. Comparison of ASE with in-cell cleanup and the QuEChERS sample preparation methods for the analysis of pesticide residues in tea [J]. Int Food Res J, 2017, 24(1): 261–267.

[9] Duodu GO, Goonetilleke A, Ayoko GA. Optimization of in-cell accelerated solvent extraction technique for the determination of organochlorine pesticides in river sediments [J]. Talanta, 2016, 150: 278–285.

[10] Sanchez AG, Martos NR, Ballesteros E. Multiresidue analysis of pesticides in olive oil by gel permeation chromatography followed by gas chromatography–tandem mass-spectrometric determination [J]. Anal Chim Acta, 2006, 558(1): 53–61.

[11] David F, Devos C, Dumont E, *et al*. Determination of pesticides in fatty matrices using gel permeation clean-up followed by GC-MS/MS and LC-MS/MS analysis: a comparison of low-and high-pressure gel permeation columns [J]. Talanta, 2017, 165: 201–210.

[12] Garrido-Frenich A, Fernandez-Moreno JL, Martinez-Vidal JL, *et al*. Application of gas chromatography coupled to triple quadruple mass

spectrometry for the multiresidue analysis of pesticides in olive oil [J]. J Agric Food Chem, 2007, 55(21): 8346–8352.

[13] Lozowicka B, Rutkowska E, Hrynko I. Simultaneous determination of 223 pesticides in tobacco by GC with simultaneous electron capture and nitrogen-phosphorous detection and mass spectrometric confirmation [J]. Open Chem, 2015, 13(1): 1137–1149.

[14] Machado I, Gerez N, Piston M, et al. Determination of pesticide residues in globe artichoke leaves and fruits by GC–MS and LC–MS/MS using the same QuEChERS procedure [J]. Food Chem, 2017, 227: 227–236.

[15] Gilbert-Lopeza B, Garcia-Reyesa JF, Fernandez-Albab AR, et al. Evaluation of two sample treatment methodologies for large-scale pesticide residue analysis in olive oil by fast liquid chromatography-electrospray mass spectrometry [J]. J Chromatogr A, 2010, 1217(24): 3736–3747.

[16] Wu CC. Multiresidue method for the determination of pesticides in oolong tea using QuEChERS by gas chromatography-triple quadrupole tandem mass spectrometry [J]. Food Chem, 2017, 229: 580–587.

[17] Abdel-Ghany MF, Hussein LA, Azab NFE, et al. Simultaneous determination of eight neonicotinoid insecticide residues and two primary metabolites in cucumbers and soil by liquid chromatography–tandem mass spectrometry coupled with QuEChERS [J]. J Chromatogr B, 2016, 1031: 15–28.

[18] Islam AKMM, Hong SM, Lee HS, et al. Identification and characterization of matrix components in spinach during QuEChERS sample preparation for pesticide residue analysis by LC–ESI–MS/MS, GC–MS and UPLC-DAD [J]. J Food Sci Technol, 2018, 55(10): 3930–3938.

[19] 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.

[20] Lehotay SJ. Determination of pesticide residues in foods by acetonitrile extraction and partitioning with magnesium sulfate: collaborative study [J]. J AoAC Int, 2007, 90(2): 485–520.

[21] European Committee for Standardization (CEN) Standard Method EN 15662. Foods of plant origin-determination of pesticide residues using GC-MS and/or LC-MS/MS following acetonitrile extraction partitioning and cleanup by dispersive SPE-QuEChERS-method [S].

[22] Wang JS, He ZY, Wang L, et al. Automatic single-step quick, easy, cheap, effective, rugged and safe sample preparation devices for analysis of pesticide residues in foods [J]. J Chromatogr A, 2017, 1521: 10–18.

[23] Guo JG, Tong MM, Tang J, et al. Analysis of multiple pesticide residues in polyphenol-rich agricultural products by UPLC-MS/MS using a modified QuEChERS extraction and dilution method [J]. Food Chem, 2019, 274: 452–459.

[24] Villalba AM, Vaclavik L, Moyano E, et al. Direct analysis in real time high-resolution mass spectrometry for high-throughput analysis of antiparasitic veterinary drugs in feed and food [J]. Rapid Commun Mass Spectrom, 2013, 27: 467–475.

[25] Kang J, Fan CL, Chang QY, et al. Simultaneous determination of multi-class veterinary drug residues in different muscle tissues by modified QuEChERS combined with HPLC-MS/MS [J]. Anal Methods, 2014, 6: 6285–6293.

[26] Sapozhnikova Y. High-throughput analytical method for 265 pesticides

and environmental contaminants in meats and poultry by fast low pressure gas chromatography and ultrahigh-performance liquid chromatography tandem mass spectrometry [J]. J Chromatogr A, 2018, 1572: 203–211.

[27] Tsai HK, Chen S, Huang CW, et al. Occurrence and exposure to polycyclic aromatic hydrocarbons in kindling-free-charcoal grilled meat products in Taiwan [J]. Food Chem Toxicol, 2014, 71: 149–158.

[28] Madureira TV, Velhote S, Santos C, et al. A step forward using QuEChERS (quick, easy, cheap, effective, rugged, and safe) based extraction and gas chromatography-tandem mass spectrometry–levels of priority polycyclic aromatic hydrocarbons in wild and commercial mussels [J]. Environ Sci Pollut Res Int, 2014, 21: 6089–6098.

[29] Jia W, Chu XG, Ling Y, et al. Multi-mycotoxin analysis in dairy products by liquid chromatography coupled to quadrupole orbitrap mass spectrometry [J]. J Chromatogr A, 2014, 1345: 107–114.

[30] Koesukwiwat U, Sanguankaew K, Leepipatpiboon N. Evaluation of a modified QuEChERS method for analysis of mycotoxins in rice [J]. Food Chem, 2014, 153: 44–51.

[31] Plossl F, Giera M, Bracher F. Multiresidue analytical method using dispersive solid-phase extraction and gas chromatography/ion trap mass spectrometry to determine pharmaceuticals in whole blood [J]. J Chromatogr A, 2006, 1135: 19–26.

[32] Abdallah H, Amaudguilhem C, Jaber F, et al. Multiresidue analysis of 22 sulfonamides and their metabolites in animal tissues using quick, easy, cheap, effective, rugged, and safe extraction and high resolution mass spectrometry (hybrid linear iontrap-orbitrap) [J]. J Chromatogr A, 2014, 1355: 61–72.

[33] Tienstra M, Mol HGJ. Application of gas chromatography coupled to quadrupole-orbitrap mass spectrometry for pesticide residue analysis in cereals and feed ingredients [J]. J AoAC Int, 2018, 101(2): 342–351.

[34] Gonzalez-Curbelo MÁ, Socas-Rodriguez B, Herrero M, et al. Dissipation kinetics of organophosphorus pesticides in milled toasted maize and wheat flour (gofio) during storage [J]. Food Chem, 2017, 229: 854–859.

[35] Parrilla VP, Hakme E, Ucles S, et al. Large multiresidue analysis of pesticides in edible vegetable oils by using efficient solid-phase extraction sorbents based on quick, easy, cheap, effective, rugged and safe methodology followed by gas chromatography-tandem mass spectrometry [J]. J Chromatogr A, 2016, 1463: 20–31.

[36] Manav OG, Dinc-Zor S, Alpdogan G. Optimization of a modified QuEChERS method by means of experimental design for multiresidue determination of pesticides in milk and dairy products by GC–MS [J]. Microchem J, 2019, 144: 124–129.

[37] Rejczak T, Tuzimski T. QuEChERS-based extraction with dispersive solid phase extraction clean-up using PSA and ZrO_2-based sorbents for determination of pesticides in bovine milk samples by HPLC-DAD [J]. Food Chem, 2017, 217: 225–233.

[38] Dd-Oliveira-Arias JL, Rombaldi C, Caldas SS, et al. Alternative sorbents for the dispersive solid-phase extraction step in quick, easy, cheap, effective, rugged and safe method for extraction of pesticides from rice paddy soils with determination by liquid chromatography tandem mass spectrometry [J]. J Chromatogr A, 2014, 1360: 66–75.

[39] Nasution L, Purba E, Munir E, et al. Biochemical identification of bacteria in polluted soil from Merdeka Village, Merdeka District, Karo Regency [J]. Int J Adv Res, 2016, 4(9): 1719–1723.

[40] Moreno-Gonzalez D, Alcantara-Duran J, Addona SM, et al. Multi-residue

pesticide analysis in virgin olive oil by nanoflow liquid chromatography high resolution mass spectrometry [J]. J Chromatogr A, 2018, 1562: 27–35.

[41] Gil-Garcia MD, Martinez-Galera M, Ucles S, *et al*. Ultrasound-assisted extraction based on QuEChERS of pesticide residues in honeybees and determination by LC-MS/MS and GC-MS/MS [J]. Anal Bioanal Chem, 2018, 410(21): 5195–5210.

[42] Barganska Z, Olkowska E, Dymerski T, *et al*. Determination of pesticide residues in honey using the GC×GC-TOF-MS technique [J]. J Bioprocess Biotech, 2014, 4(7): 1–5.

[43] Stockelhuber M, Muller C, Vetter F, *et al*. Determination of pesticides adsorbed on arthropods and gastropods by a micro-QuEChERS approach and GC-MS/MS [J]. Chromatographia, 2017, 80(5): 825–829.

[44] Li MM, Dai C, Wang FZ, *et al*. Chemometric-assisted QuEChERS extraction method for post-harvest pesticide determination in fruits and vegetables [J]. Sci Rep, 2017, 7(1): 42489–42501.

[45] Maestroni B, Abu-Alnaser A, Ghanem I, *et al*. Validation of an analytical method for the determination of pesticide residues in vine leaves by GC-MS/MS [J]. J Agric Food Chem, 2018, 66(25): 6421–6430.

[46] Faraji M, Noorbakhsh R, Shafieyan H, *et al*. Determination of acetamiprid, imidacloprid, and spirotetramat and their relevant metabolites in pistachio using modified QuEChERS combined with liquid chromatography-tandem mass spectrometry [J]. Food Chem, 2018, 240: 634–641.

[47] Min ZW, Hong SM, Yang IC, *et al*. Analysis of pesticide residues in brown rice using modified QuEChERS multiresidue method combined with electrospray ionization-liquid chromatography-tandem mass spectrometric detection [J]. J Korean Soc Appl Biol Chem, 2012, 55: 769–775.

[48] Mol HGJ, Rooseboom A, Van-Dam R, *et al*. Modification and re-validation of the ethyl acetate-based multi-residue method for pesticides in produce [J]. Anal Bioanal Chem, 2007, 389(6): 1715–1754.

[49] Volpatto F, Wastowski AD, Bemardi G, *et al*. Evaluation of QuEChERS sample preparation and gas chromatography coupled to mass spectrometry for the determination of pesticide residues in grapes [J]. J Braz Chem Soc, 2016, 27(9): 1533–1540.

[50] Viera MS, Rizzetti TM, De-Souza MP, *et al*. Multiresidue determination of pesticides in crop plants by the quick, easy, cheap, effective, rugged, and safe method and ultra-high-performance liquid chromatography tandem mass spectrometry using a calibration based on a single level standard addition in the sample [J]. J Chromatogr A, 2017, 1526: 119–127.

[51] European Commission DG-SANTE. Document SANTE/11945/2015. Method validation and quality control procedures for pesticide residue analysis in food and feed [S].

[52] Li SS, Liu XG, Dong FS, *et al*. Chemometric-assisted QuEChERS extraction method for the residual analysis of thiacloprid, spirotetramat and spirotetramat's four metabolites in pepper: application of their dissipation patterns [J]. Food Chem, 2016, 192: 893–899.

[53] Qin YH, Zhang JR, Li YF, *et al*. Automated multi-filtration cleanup with nitrogen-enriched activated carbon material as pesticide multi-residue analysis method in representative crop commodities [J]. J Chromatogr A, 2017, 1515: 62–68.

[54] Huang YS, Shi T, Luo X, *et al*. Determination of multi-pesticide residues in green tea with a modified QuEChERS protocol coupled to HPLC-MS/MS [J]. Food Chem, 2019, 275: 255–264.

[55] Zhan XP, Ma L, Huang LQ, *et al*. The optimization and establishment of QuEChERS-UPLC–MS/MS method for simultaneously detecting various kinds of pesticides residues in fruits and vegetables [J]. J Chromatogr B, 2017, 1060: 281–290.

[56] Da-Costa-Morail EH, Collins CH, Jardim ICSF. Pesticide determination in sweet peppers using QuEChERS and LC-MS/MS [J]. Food Chem, 2018, 249: 77–83.

[57] Lehmann E, Oltramare C, De-Alencastro LF. Development of a modified QuEChERS method for multi-class pesticide analysis in human hair by GC-MS and UPLC-MS/MS [J]. Anal Chim Acta, 2018, 999: 87–98.

[58] Moreno-Gonzalez D, Huertas-Perez JF, Garcia-Campana AM, *et al*. Determination of carbamates in edible vegetable oils by ultra-high performance liquid chromatography–tandem mass spectrometry using a new clean-up based on zirconia for QuEChERS methodology [J]. Talanta, 2014, 128: 299–304.

[59] Dusek M, Jandovska V, Olsovska J. Analysis of multiresidue pesticides in dried hops by LC-MS/MS using QuEChERS extraction together with dSPE clean-up [J]. J Brew, 2018, 124(3): 222–229.

[60] Femandes VC, Freitas M, Pacheco JPG, *et al*. Magnetic dispersive micro solid-phase extraction and gas chromatography determination of organophosphorus pesticides in strawberries [J]. J Chromatogr A, 2018, 1566: 1–12.

[61] Ma GC, Zhang ML, Zhu L, *et al*. Facile synthesis of amine-functional reduced graphene oxides as modified quick, easy, cheap, effective, rugged and safe adsorbent for multi-pesticide residues analysis of tea [J]. J Chromatogr A, 2018, 1531: 22–31.

[62] Martins ML, Kemmeric M, Prestes OD, *et al*. Evaluation of an alternative fluorinated sorbent for dispersive solid-phase extraction clean-up of the quick, easy, cheap, effective, rugged, and safe method for pesticide residues analysis [J]. J Chromatogr A, 2017, 1514: 36–43.

[63] Singh S, Srivastava A, Singh SP. Inexpensive, effective novel activated carbon fibers for sample cleanup: application to multipesticide residue analysis in food commodities using a QuEChERS method [J]. Anal Bioanal Chem, 2018, 410(8): 2241–2251.

[64] Trevisan MTS, Owen RW, Calatayud-Vemich P, *et al*. Pesticide analysis in coffee leaves using a quick, easy, cheap, effective, rugged and safe approach and liquid chromatography tandem mass spectrometry: optimization of the clean-up step [J]. J Chromatogr A, 2017, 1512: 98–106.

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