QuEChERS 技术净化材料在果蔬农药残留检测中的应用进展

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摘　要: 农产品中常用的农药包括有机磷、氨基甲酸酯、拟除虫菊酯、有机氯和新烟碱类, 然而农药的高毒性对消费者造成潜在的健康危害。在农药残留分析方法建立过程中开发和使用具有“绿色化学”特点的溶剂和方法一直是分析工作者努力的方向。QuEChERS 技术中基质净化步骤在农药残留分析中起着至关重要的作用。本文综述了 QuEChERS 样品制备方法在水果蔬菜等农药残留检测中的应用概况, 总结了 QuEChERS 技术常用的传统净化材料如 N-丙基乙二胺和石墨化炭黑、十八烷基键合硅胶固定相和新型净化材料如多壁碳纳米管、磁性纳米材料、氟化材料及其他新型改性材料等在农药残留检测中的应用进展, 就新型净化材料的结构特性、功能及应用进行了分析, 阐明了 QuEChERS 技术的发展趋势和前景在于开发更多操作便捷、成本低廉的新型净化材料, 有助于这一领域进一步的研究发展。

关键词: 样品制备; 农药残留; QuEChERS; 净化材料

Application progress of QuEChERS technique purify agent in pesticide residue detection of fruit and vegetables

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ABSTRACT: Pesticides from the classes of organophosphates, carbamates, pyrethroids, organochlorines and neonicotinoids have been commonly used in agricultural products. However, the high toxicity of pesticides poses a potential health hazard to consumers. Developing and using solvents and methods with the characteristics of “green chemistry” in the process of establishing methods for pesticide residue analysis has always been the direction of the efforts of analysts. The clean-up steps in QuEChERS technology play a critical role in the success of pesticide residue analysis. This paper reviewed the application progress of QuEChERS sample preparation methods in the detection of

基金项目: 国家市场监管重点实验室(热带果蔬质量与安全)基础应用研究课题项目(KF-2022011)、海南省自然科学基金资助项目(221QN0973)

Fund: Supported by the Key Laboratory of Tropical Fruits and Vegetables Quality and Safety for State Market Regulation (KF-2022011), and the Natural Science Foundation of Hainan Province (221QN0973)

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pesticide residues of fruits and vegetables, summarized the application progress of traditional purification materials commonly used in QuEChERS technique, such as N-propyl ethylenediamine and graphitized carbon black, octadecyl bonded silica gel fixed phase and new purification materials, such as multi-wall carbon nanotubes, magnetic nanomaterials, fluorinated materials and other new modified materials, in pesticide residue detection, analyzed the structural characteristics, functions and applications of the new purification materials, and clarified that the development trend and prospect of QuEChERS technology lied in the development of more convenient and low-cost new purification materials, which is conducive to further research and development in this field.

KEY WORDS: sample preparation; pesticide residues; QuEChERS; purify agent

0 引 言

近年来，食品中农药残留作为最重要的食品安全问题之一受到越来越多的关注。为了提高农产品产量、延长保质期，生产者会使用大量的农药防制害虫、杂草等[1]。农药的过度使用，加之缺乏良好的农业实践，可能会导致其在最终产品中残留，这些残留会对消费者造成潜在的健康危害，对健康的影响程度与农药残留量密切相关[2–4]。常用的农药包括有机磷类、氨基甲酸酯类、拟除虫菊酯类、有机氯类等，对农药残留进行检验检测是保证食用农产品安全的重要手段和重要技术支撑。因此，农药残留量的准确测定显得尤为重要。通常采用色谱法进行农药残留的定量分析，包括气相色谱法(gas chromatography, GC)、液相色谱法(liquid chromatography, LC)、液相色谱-串联质谱法(liquid chromatography-tandem mass spectrometry, LC-MS/MS)、气相色谱-串联质谱法(gas chromatography-tandem mass spectrometry, GC-MS/MS)。在色谱分析检测中，分析物信号会受到样品和共萃取物性质的影响，呈现出一定程度的信号抑制或增强，这种影响的程度随基质和化合物类型的不同而不同[5–6]。与分析物具有相同或相似保留时间的基质成分会对检测信号造成干扰，影响检验方法的准确性，可能导致分析物峰的掩蔽(阴性结果)，或者被识别为现实中不存在的分析物(假阳性峰)，这种非待测组分对待测物浓度或质量测定准确度的影响被称为基质效应[7–8]。消除基质效应就是在适当的水平上分离和浓缩目标分析物，并从样品基质中去除可能的干扰物质，从而减少或消除样品的干扰[9–10]。但由于新型农药不断引入市场，加之基质的复杂性和样品中农药的微量水平，消除基质效应、准确测定食品基质中的农药含量并不容易。在这种背景下，需要开发合适、廉价、敏感的分析技术，以方便高效的方式监测农药残留。

2003 年，ANASTASSIADES 等[11]提出了一种快速(quick)、简单(easy)、便宜(cheap)、有效(effective)、可靠(rugged)、安全(safe)提取食品中农药残留的方法即 QuEChERS 技术。该技术是将均质后的样品经提取液提取，使用萃取盐盐析分层，根据基质分散萃取机制，通过净化材料与基质中绝大多数干扰物(如有机酸、脂肪酸、碳水化合物等)结合，再经离心分层，取上层液进行分析。与传统的固相萃取相比，QuEChERS 方法减少了溶剂交换、反复淋洗和洗脱、重复净化筛选等步骤，极大程度上缩减时间，提高了回收率[12–13]。自 QuEChERS 技术提出后，许多研究者就其发展历程、方法改进(萃取溶剂、盐析盐、吸附剂及配比等)、应用基质(水果、蔬菜、谷物、动物性产品等)、应用领域(农药残留检测、兽药残留检测、真菌毒素检测、多环芳烃检测等)、分析技术(GC、GC-MS/MS、LC 等)等方面进行过综述[14–17]。QuEChERS 技术中可以根据被测物的性质选用相应的净化材料,以达到最优的净化效果,这是近年来农药残留检测技术的研究热点[18]。但目前尚缺少关于不同净化材料方面的全面综述。本文就近年来 QuEChERS 技术所用净化材料在水果蔬菜等农药残留检测中的应用进行综述与展望，以便于这一领域进一步的研究与突破。

1 QuEChERS 技术概述

QuEChERS 早期方法出现后，研究者在复杂基质中对多种农药进行了反复分析论证，2007—2008 年国际上产生两种官方的标准，美国农业部通用标准 AOAC 2007.01 和欧盟标准 EN 15662:2008[19]。这两种官方的标准与早期方法的区别在于 QuEChERS 提取过程中添加了柠檬酸和醋酸盐，营造一种缓冲盐体系以适应更为广泛的酸碱环境并适用于 pH 敏感性农药[20]。QuEChERS 方法由于其优良的回收、富集和提取能力，已广泛用于土壤、鱼类、肉类、乳制品、茶、中草药、油料、水果和蔬菜等基质中的农药残留分析[21–27]。近年来，基于 QuEChERS 方法的农药残留检测技术得到了广泛研究和持续性改进，包括缓冲调节 pH、萃取溶剂、吸水盐、净化剂和分析仪器等方面[28–31]。这些改进大多是为了在不同复杂度的基质中获得较高的回收率，以避免农药降解和减少基质效应，减少预分离步骤的时间，经济环保。目前，对不同 QuEChERS 方法进行评价的指标包括回收率、精密度、基质效应等，但由于基质和农药分析物的复杂性，尚没有能适用于所有农药残留分析的单一评价方法。影响 QuEChERS 方法的关键

在于分析物与基质的相互作用, 因此, 在样品预处理程序中经适当的分离和浓缩目标分析物, 采用合适的净化剂去除样品基质中可能的干扰, 对于实现色谱分析的准确定量至关重要。在预处理过程中, 吸附剂(即净化材料)的选择十分重要, 未来 QuEChERS 技术的改进重点也在于此。

2　传统净化材料

QuEChERS 技术常用的传统净化材料包括 N-丙基乙二胺(primary secondary amines, PSA)、十八烷基键合硅胶固定相(octadecylsilane, C_{18})和石墨化炭黑(graphitized carbon black, GCB)[32]。在农药残留色谱检测中, 基质效应比较强的样品有鳄梨(高脂肪含量)、橙子(高酸含量)、韭菜(硫化物含量高)和欧芹(高叶绿素化合物)等。韭菜和鳄梨中的硫化物或脂肪, 可分别与农药产生较强的相互作用, 在气相色谱检测中表现出强基质干扰; 西兰花在液相色谱中表现出强基质干扰[33]。应对不同的基质, PSA、GBC 和 C_{18} 的净化效果存在一些不足, 通常选择联合使用规避各自的弊端。

2.1　PSA

PSA 是一种弱阴离子交换吸附剂, 含有两个氨基(伯胺和仲胺), p*K*a 值分别为 10.1 和 10.9, 具有极性相互作用和弱阴离子交换作用。PSA 通常用于从非极性样品中去除各种极性有机酸、极性色素、糖、脂肪酸和其他一些形成氢键的基质共提取物, 是 QuEChERS 技术主要的净化吸附材料[34–35]。LI 等[36]在 QuEChERS 预处理程序中采用 PSA 净化剂联合超高效液相色谱-串联质谱法(ultra performance liquid chromatography-tandem mass spectrometry, UPLC-MS/MS)分析监测了柑橘类(包括柑、橘、橙)水果中 106 种农药的残留情况, 并开展了农药残留的健康风险评估, 可用于指导柑橘类水果的农药使用和田间管理。虽然, PSA 能够有效地去除酸性水果中的杂质, 可以作为净化剂单独应用于柑橘类水果中, 但是其对色素的净化不够彻底, 因此, 在 QuEChERS 技术净化材料选择时, PSA 通常与其他材料联合使用。BIBI 等[37]采用 PSA−C_{18} 联合使用优化了 QuEChERS 净化条件, 分析了柑橘类水果中 51 种农药残留。在该方法中, C_{18} 的掺入能够明显降低色谱信号干扰, 达到很好的净化效果, 且 49 种农药的回收率在可接受的范围内。然而, PSA 清理性能并不总是令人满意, 使用量过大时会吸附强极性的目标分析物, 如甜菜安、辛菌胺等, 导致其回收率降低[38–39]。PSA 的氨基还可与酸性农药中的羧酸基(-COOH)相互作用导致对酸性农药的吸附, 不利于酸性农药的基质净化[40–42]。

2.2　GCB

GCB 常用作去除不同基质的色素, 例如平面结构的叶绿素、类胡萝卜素、番茄红素、多酚类等, 然而, 它容易吸附一些平面结构的农药, 通常与其他类型净化材料联合使用以增强基质中色素的净化效果[14,43–44]。MANDAL 等[45]采用 PSA−GCB 联合使用清除香蕉中的杂多糖和类胡萝卜素, 有效降低了基质干扰。GUEDES 等[46]以番石榴作为研究基质, 对 QuEChERS 净化过程进行了优化, 在 PSA 的基础上添加了极少量的 GCB, 提取液的颜色变为无色, 提高了净化效果, 消除了21种农药的基质效应。MARTINS 等[47]研究分析了 GCB 的使用量对芒果中的色素净化作用, 发现 GCB 使用量的增加能加强基质的净化效果, 但由于其带有芳香性的正六元环平面分子结构, 会吸附平面环状目标物质, 如百菌清、六氯苯、敌敌畏、嘧霉胺等, 导致目标物的损失。GCB 的含量对色素净化效果和平面结构农药的回收率均有显著影响, 因此, GCB 的使用量对分析方法的有效性起到了决定性作用, 在农药残留检测方法的建立过程中要着重考虑。

2.3　C_{18}

C_{18} 是一种非选择性吸附剂, 可以用来吸附脂肪等含长碳链的非极性化合物, 在含脂基质中表现出较好的净化效果, 对亲脂性农药的痕量分析具有明显作用[48]。鳄梨、亚麻籽、花生和杏仁等基质中富含脂肪, 检测该种基质中亲脂性农药(脱叶亚磷、氟胺氰菊酯、醚菊酯、六氯苯、毒死蜱、狄氏剂等)是比较困难的[49]。据悉, 鳄梨(牛油果)中脂肪含量达到 10%~30%, 另外含有一些特性成分如棕榈油酸、油酸、甾醇、植醇、棕榈酸甲酯等[49–50]。CHAMKASEM 等[50]采用 $MgSO_4$−PSA−C_{18} 吸附净化组合分析了鳄梨中 136 种农药残留情况, 发现 PSA 以较弱的阴离子交换机制吸附了乙腈提取物中的脂肪酸, 非极性吸附剂 C_{18} 吸附了亲脂性干扰物和脂肪酸残留物。与 PSA 单独使用相比, C_{18} 能吸附乙腈中残留的脂肪酸和脂质残留, 提高了亲脂性农药的回收率。

3　新型净化材料

传统的 QuEChERS 技术往往需要多步离心分离, 严重影响了批量样品的预处理速度, 针对复杂基质存在富集倍数低、检出限高的缺陷。近年来许多研究者对新型净化材料进行研究, 开发出了多壁碳纳米管材料、磁性纳米材料、氟化材料及其他新型改性材料等作为吸附剂应用在样品预处理中, 简化了前处理程序, 在果蔬农药残留检测中应用比较突出[51–54]。

3.1　多壁碳纳米管材料

多壁碳纳米管(multi-walled carbon nanotubes, MWCNTs)及其聚合物功能化修饰材料具有独特的结构和性能, 高比表面积, 多层中空结构, 能通过 π-π 和疏水相互作用有效吸附色素, 可针对性的清除基质中的干扰成分[55–57], 其净

化作用类似于 GCB, 对辣椒素、胡萝卜素等干扰物质净化效果良好[57−58]。HAN 等[39]针对辛菌胺脂溶性高、表面吸收性强、多氨基等物理化学特性, 对比了 PSA、C_{18}、GCB、多壁碳纳米管和中性氧化铝(Al_2O_3)预处理测定辛菌胺净化效果, 开发了 MWCNTs 作为净化剂分析测定辛菌胺残留物的方法, 为国内辛菌胺检测方法提供了参考和支持[59]。HAN 等[60]还对比了 PSA、GCB 和 MWCNTs 对豇豆中色素的清除效果, 发现 PSA 净化效果较差, MWCNTs 的色素清除效果最好。但是由于多壁碳纳米管平面石墨烯层结构的强 π-π 堆积, 使用多壁碳纳米管作为净化材料, 会导致嘧霉胺、吡氟草胺、喹禾灵等平面结构农药的吸附[57,60]。近年来, 国内外涌现大量基于 QuEChERS 技术的多壁碳纳米管应用和功能化改进的报导。

WANG 等[61]采用金属盐共沉淀法制备了支链聚乙烯亚胺和纳米级硫酸钙功能化多壁碳纳米管(self-separating b-PEI@c-MWCNTs@$CaSO_4$, ssBPCM)。聚乙烯亚胺富含羧基和氨基, 共交联后改变了多壁纳米管的表面特性, 改善了以往多壁纳米管对平面结构农药的吸附。ssBPCM 可以有效地规避 MWCNTs 吸附平面农药的局限性。与 PSA 相比, ssBPCM 对长烷基酸、酯类和甾醇具有良好的清除效果, 可以用于降低不同果蔬中农药残留检测的基质效应影响。

3.2 磁性纳米材料

将磁性纳米颗粒(magnetic nanoparticles, MNPs)作为 QuEChERS 预处理吸附净化材料, 研究发现, 其可以被外部磁体吸引而与提取液分离, 从而减少净化剂使用量、简化样品前处理程序, 降低成本, 提高经济效益、环保效益, 进一步促进高通量检测, 甚至可以取代传统净化材料, 目前已在食品农药分析检测中得到广泛应用[53,62]。

LI 等[62]采用化学沉淀法在 $FeCl_3·6H_2O$ 和 $FeCl_2·4H_2O$ 溶液中加入沉淀剂氨水制备了 Fe_3O_4 磁性纳米颗粒, 该材料接近球形、粒径均匀、形状规则, 具有较大的比表面积和良好的分散性, 与 GCB/PSA 联合使用能够更好地清除色素干扰, 并能够避免 GCB 用量过大导致对平面结构农药的吸附。连玉晶等[63]在 LI 等[62]研究的基础上, 采用化学共沉淀法及硅烷化反应制备了 3-[2-(2-氨基乙基氨基)乙基氨基]丙基功能化四氧化三铁磁性纳米粒子{3-[2-(2-aminoethylamino) ethylamino] propyltrimethoxy functional iron oxide, Fe_3O_4@SiO_2-PAAA}, 与 PSA 相比, 该纳米颗粒在结构上多 1 个氨基, 对脂肪酸、有机酸、糖类和花青素等杂质的吸附能力会更强。YU 等[64]建立了一种基于 Fe_3O_4 磁性纳米颗粒的 QuEChERS 分散液-液微萃取方法, 该方法采用 PSA、炭黑和 Fe_3O_4 磁性纳米颗粒作为吸附剂去除绿叶蔬菜中的基质效应, 可以有效地去除基质中的脂肪酸、糖和蛋白质, 并能实现快速、高效的分离回收。该方法中的炭黑能够有效替代昂贵的 GCB(商业 GCB 的成本约为 11~12 美元每克[65]), 且不影响回收率。改性的复合磁性碳纳米材料如有机胺功能化磁性多壁碳纳米管, 能有效地去除酚类、酯类、有机酸类和醇类, 在韭菜和黄瓜等基质中分别表现出良好的降低基质效应的能力。YUAN 等[66]将 Fe_3O_4 磁性纳米颗粒与碳纳米管结合制成磁性碳纳米管(magnetic carbon nanotube, M-CNT), 进而加入十八烷胺(n-octadecylamine, ODA)进行功能化改造, 首次制备出了十八烷胺功能化磁性多孔碳纳米管(n-octadecylamine functionalized magnetic carbon nanotube porous nanocomposite, M-CNTs/ODA), 并将其作为 QuEChERS 预处理净化材料。M-CNTs/ODA 的合成机制见图 1[66]。经过对比 M-CNTs/ODA、C_{18}、GCB 和 PSA 在韭菜基质中的去基质干扰能力后, 发现 M-CNTs/ODA 降低韭菜基质效应的能力最强。M-CNTs/ODA 在磁性纳米颗粒表面的化学键可以保证其吸附时的稳定性, 每次使用后, 经乙腈溶液洗涤至少可重复使用 15 次, 且不会损失吸附能力。该材料萃取效率高、富集率高、剂量低, 与传统的方法相比, 吸附剂可以通过外部磁场从乙腈溶液中分离出来, 无需经过离心或过滤, 方法简便、灵敏、快速、高效, 极大程度上缩短了前处理时间。

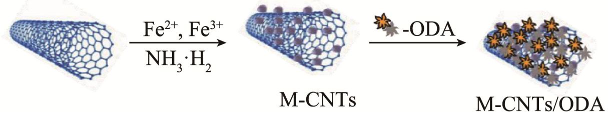

图 1 M-CNTs/ODA 的合成
Fig.1 Synthesis of M-CNTs/ODA

磁性四乙烯五胺功能化的多壁碳纳米管(magnetic tetraethylenepentamine modified multi-walled carbon nanotubes, M-TP-MWCNTs)作为净化剂可以有效地吸附醇类、有机酸和有机胺, 对基质敏感性农药二嗪磷、杀螟硫磷、香豆磷表现出很好的去基质干扰能力, M-TP-MWCNTs 的色素净化效果优于 C_{18}、PSA 单独使用以及两者的结合使用, 可将二嗪磷、杀螟硫磷、香豆磷在黄瓜基质中基质效应降低到 −11.1%至 14.8%, 极大程度消除基质干扰[67]。M-TP-MWCNTs 可以通过施加外部磁场快速回收, 简化预处理操作, 净化过程可以在 2 min 内完成, 净化时间短, 便于高通量分析[67−68]。

有机胺功能化磁性多壁碳纳米管, 组成元素多为碳、氧、氮, 突显了氨基、羧基的结构特性, 增强了材料的极性, 结合碳纳米管的中空结构和 Fe_3O_4 磁性能, 表现出更优异的净化性能, 并通过磁分离简化了预处理操作步骤, 实现了磁体的快速分离, 由于该材料吸附时的稳定性强, 可以被重复使用, 也提升了经济效益[66−67]。常见的 Fe_3O_4 磁性纳米颗粒作为 QuEChERS 技术净化材料的应用及分离流程见图 2[66]。

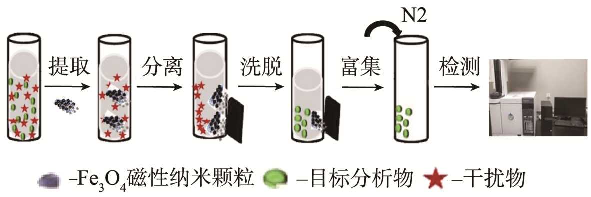

图 2　Fe_3O_4 磁性纳米颗粒的应用及分离
Fig.2　Application and separation of the Fe_3O_4 magnetic nanoparticles

3.3　氟化材料

壳聚糖(chitosan，CTS)是一种可再生、可降解、资源丰富的天然生物聚合物，其含有可形成氢键相互作用和静电相互作用的氨基、羟基等活性基团，但是由于壳聚糖机械性能较差、在酸性环境中易于降解等缺陷，限制了它的广泛应用[69–70]。全氟丙酸酐修饰的氟化壳聚糖(fluorinated methacrylamide chitosan, MACF)中存在 C-F、–CF3、$–CF_2$ 基团，能够增强壳聚糖的极性和吸附选择性，作为净化剂时对基质中的干扰成分有很好的吸附作用[71]。氟化后的壳聚糖具有极大的电负性，提高了净化剂的清理性能，这表明，氟化是提高清理效率的有效途径。人参是一种非常复杂的基质，含有大量的人参皂苷、氨基酸、挥发油、多糖等，MACF 作用于人参基质中表现出很好的净化效果。这种改性壳聚糖作为复杂基质中绝大多数目标农药预处理的净化剂具有广泛应用前景[71–73]。氟化壳聚糖具有使用剂量少、绿色环保等特点，为壳聚糖用途开发和甲壳素的利用提供了新思路。

氟基材料对脂肪类化合物具有较好的选择性。WANG 等[74]使用多壁碳纳米管、Fe_3O_4 纳米颗粒、2,2,2-三氟乙基胺为原料制备了磁性氟化多壁碳纳米管(magnetic fluorinated multi-walled carbon nanotubes, M-F-MWCNTs)，可以有效地去除基质中黄酮类、酚类、有机酸、有机胺等，清理性能优于 C_{18} 和 PSA。采用磁性氟化多壁碳纳米管净化剂改进的 QuEChERS 农药残留检测方法操作简单、快捷，有望广泛应用于复杂基质样品中的农药分析检测。邓奇林[75]开发的甲基丙烯酸三氟乙酯修饰的氟化壳聚糖聚合物，表面有许多的孔隙，比表面积增大，对杂质的吸附能力增强，该聚合物应用于 QuEChERS 中去除苹果基质中杂质干扰达到良好的效果，实现了农药残留的快速分离和检测。

3.4　其他新型改性材料

酚醛树脂基活性炭纤维(phenolic resin based activated carbon fibers, ACFs)表面光滑、均匀、具有多孔性(介孔和大孔)，具有 C≡C、C=O 和 O-H 官能团，这些官能团会与干扰基质相互作用，增强清理性能。ACFs 由于其纤维状结构、高孔隙、大容量，具有优异的填充密度、快速的吸附动力学、良好的多孔存储能力和易于处理等特点，是目前最重要的纤维炭材料之一[76]。研究表明，ACFs 对色素有良好的清除效果，且能够重复利用，可作为 QuEChERS 技术中 PSA 的替代品。ACFs 作为分散固相萃取中的净化剂作用在花椰菜、黄瓜、香蕉、苹果、麦、小麦和黑豆基质中，与 PSA 净化效果相当[77]。与 PSA 相比，少量廉价的 ACFs 对色素就有良好的清除效果，可以达到净化目的，且能够重复利用，可作为 QuEChERS 法中 PSA 的替代品，用于吸附剂组合中快速筛选，并指导开发新型高效吸附剂[78–79]。

氮掺杂石墨化碳是一种重要的二维层状材料，叶学敏[80]将氮掺杂石墨化碳(双氰胺工业废渣回收再利用产品)和低共熔溶剂分别作为 QuEChERS 方法中的新型吸附剂和萃取溶剂，建立了一种新型 QuEChERS-GC-MS/MS 方法，对番茄中 27 种有机氯和拟除虫菊酯农药残留进行了分析，取得了满意结果。

3.5　新型净化材料的应用

多壁碳纳米管、磁性纳米材料、功能化壳聚糖等新型净化材料，由于其结构特点具有吸附性能，在此基础上进一步经过有机胺化、氟化等功能化的改进和优化，规避了基础材料在净化过程中的弊端和不足，能够去除复杂基质中的色素、有机酸、脂类、多糖等化合物的干扰，消除基质效应，在基于 QuEChERS 方法的农药残留检测前处理过程中应用前景广阔。

表 1 进一步总结了基于 QuEChERS 预处理技术的新型吸附净化材料在农药残留检测中的应用，可为今后开展新型吸附净化材料研究及应用提供参考。

4　结束语

分析比较国内外基于 QuEChER 方法的食用农产品农药残留的研究进展，发现目前对于消除基质效应的方法尚缺乏系统、全面的数据支持。面向未来，需要不断探索建立应对特殊基质和敏感农药的新型 QuEChERS 方法来消除基质效应，提高农药残留分析的准确性。

目前应用于农药残留的样品预处理方法尚不理想，传统的样品预处理方法通常是多阶段的程序，增加了前处理的成本，延长了分析检测周期，不利于批量样品检测。结合当前的研究现状，应用新型材料以及在净化过程中添加磁性材料等方式，使样品预处理方法更简单、更高效、更快速，从而有利于高通量分析，对这些新材料的食品安全评估和研究也将更加深入，是未来一段时期内的研究重点。

目前，无论是传统的净化材料还是新开发的部分纳米材料包括二氧化硅基材料、碳纳米管基材料、石墨烯基材料等，都不同程度存在价格昂贵，而且合成成本较高等问题，因此，进一步研究开发出更低成本的、容易获得的、有效的吸附剂也是今后的一个重要研究方向。

表 1 基于 QuEChERS 预处理技术的新型净化材料在农药残留检测中的应用
Table 1 Applications of new purification materials in QuEChERS method for the pesticides analysis

基质	净化材料	分析技术	目标农药	参考文献
豇豆	MWCNTs	GC–MS/MS	171 种农药: 灭多威、异丙威、敌敌畏、乙酰甲胺磷、甲拌磷、乐果、联苯菊酯、腐霉利等	[60]
卷心菜、橙子、苹果、黄瓜	ssBPCM	GC–MS/MS	28 种农药包括有机磷类、氨基甲酸酯类、和拟除虫菊酯类等	[61]
番茄、黄瓜、橙子、苹果	MNPs	GC–MS/MS	101 种农药: 敌敌畏、杀虫脒、杀螟硫磷、对硫磷、杀扑磷等	[62]
番茄、黄瓜、苹果	Fe_3O_4@SiO_2-PAAA	GC–MS/MS	7 种农药: 猛杀威、二嗪磷、百菌清、硫丹等	[63]
黄瓜、韭菜、菠菜、辣椒、橙子	M-CNTs/ODA	GC–MS	16 中农药: 毒死蜱、对硫磷、杀扑磷、 三唑磷、三唑酮等	[66]
黄瓜	M-TP-MWCNTs	GC–MS	10 种有机磷农药: 二嗪磷、马拉硫磷、对硫磷、杀螟硫磷、香豆磷、伏杀硫磷等	[67]
人参	MACF	GC–MS/MS	20 种有机磷农药: 敌敌畏、氧乐果、甲基对硫磷, 三唑磷等	[71]
黄瓜、花椰菜、香蕉、苹果	ACFs	GC–MS/MS	26 种农药(包括有机磷、有机氯、拟除虫菊酯和除草剂): 敌敌畏、甲拌磷、毒死蜱、 氯氰菊酯等	[77]

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(责任编辑: 韩晓红　黄周梅)

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