分散液液微萃取技术在农药残留分析中的应用概述

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摘 要: 目前农药残留问题已成为全社会关注的热点, 发展快速、可靠和环境友好的农药残留前处理检测技术, 对于合理使用农药、保护环境和保障人类健康具有重要意义。分散液液微萃取(dispersive liquid-liquid microextraction, DLLME)是 2006 年发展起来的一种新型的液液微萃取技术, 具有操作简单、富集倍数高、有机溶剂用量少等特点, 目前已广泛应用于农药残留的检测中。本文对分散液液微萃取在水、蔬菜水果、牛奶、酒、蜂蜜、谷物、茶叶、中药材、土壤、生物样本中农药残留检测的应用进行了综述, 并对该方法的前景进行了展望。

关键词: 分散液液微萃取; 农药残留; 样品前处理

Application of dispersive liquid-liquid microextraction in pesticide residue analysis

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ABSTRACT: At present, the problem of pesticide residues has become a hot spot for the whole society. The development of fast, reliable and environmentally friendly pesticide residue pretreatment detection technology is of great significance for the rational use of pesticides, protection of the environment and protection of human health. Dispersive liquid-liquid microextraction is a new type of liquid-liquid microextraction technology developed in 2006. It has the characteristics of simple operation, high enrichment factor, and small amount of organic solvent. At present, it has been widely used in the detection of pesticide residues. In this paper, the application of dispersive liquid-liquid microextraction in the detection of pesticide residues in water, vegetables and fruits, milk, wine, honey, cereals, tea, traditional Chinese medicines, soil, and biological samples was reviewed, and the prospects of the method were prospected.

KEY WORDS: dispersive liquid-liquid microextraction; pesticide residues; sample pretreatment

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1 引 言

分散液液微萃取(dispersive liquid-liquid microextraction, DLLME)是 Rezaee 等[1]在 2006 年提出的一种新型液液微萃取技术, 该技术基于目标分析物在样品溶液和小体积萃取剂之间的分配平衡, 相当于微型化的液液萃取。基本过程是先通过注射器向样品溶液中加入数十微升萃取剂和一定体积分散剂, 萃取后再经离心分层, 用微量进样器取出萃取剂就可直接进样分析。其原理是萃取剂在分散剂的作用下在样品溶液中形成分散的微小液滴, 形成萃取剂-分散剂-样品溶液三相乳浊液体系, 从而增大了萃取剂和目标分析物的接触面积, 使目标分析物在样品溶液及萃取剂之间快速达到分配平衡而完成萃取。

和传统的前处理方法相比, 该技术具有操作简单、快速、成本低、富集倍数高、所需有机溶剂用量少、萃取时间短等特点, 现已广泛应用于多种无机和有机化合物的提取分析。最初, DLLME 技术主要应用于较为简单的液体样品中农药残留的分析, 对复杂基质的适用性较差。近年来随着新型萃取剂(绿色溶剂离子液体[2,3], 萃取相易收集的低密度溶剂[4,5], 密度小且熔点低于常温的悬浮固化萃取剂[6,7]等)的不断涌现, 各种辅助分散模式(超声辅助[8,9]、空气辅助[10]、涡旋辅助[11,12]等)的发展, 并通过与其他成熟技术(QuEChERS[13,14]、固相萃取[15-17]、液液萃取[18]等)的结合, 使 DLLME 在农药残留检测中的应用范围更广, 萃取效率和灵敏度也明显提高, 目前已广泛应用到食品[19,20]、环境[21,22]、生物样本[23]等多种基质中农药残留的检测。本文对分散液液微萃取在水、蔬菜水果、牛奶、酒、蜂蜜、谷物、茶叶、中药材、土壤、生物样本中农药残留检测的应用进行了综述, 并对该方法的发展趋势进行了展望, 旨在为今后研究分散液液微萃取技术在农药残留分析中的应用提供参考。

2 DLLME 在农药残留分析中的应用

2.1 水

水体中的农药残留可通过水产养殖或种植业等途径污染食品, 危及人类健康。目前水中农药残留检测最常用的样品前处理方法有液液萃取和固相萃取, 不仅方法费时费力, 且需要大量的水样与有机溶剂。DLLME 技术用于水样等基质简单的液体样品时优势尤为显著, 只需要微升级的萃取剂和几毫升的水样即可, 且操作简单快速, 目前已广泛应用于雨水、地表水、地下水等水样中农药残留的检测中。陈波等[24]建立了地表水中 34 种农药残留的 DLLME 与气相色谱-质谱联用技术 (gas chromatography-mass spectrometry, GC-MS)联用快速筛查及定量方法, 以四氯化碳(35 μL)为萃取剂, 丙酮(1 mL)为分散剂, 方法的检出限为 0.002~0.065 μg/L, 富集因子为 101~297 倍, 可见该方法有较好的富集效果。Liu 等[25]建立了 DLLME 与 HPLC(high performance liquid chromatography)快速测定水样中 5 种氨基甲酸酯农药的分析方法, 以三氯甲烷(40 μL)为萃取剂, 乙腈(1 mL)为分散剂, 5 种农药的检出限为 0.1~0.5 ng/mL, 富集因子为 80~177 倍, 并将该方法成功用于雨水、地表水和地下水的检测。徐仿敏等[26]采用 DLLME-GC-MS 同时快速测定鱼塘水中 24 种常见农药, 以四氯乙烯(30 μL)为萃取剂, 乙醇(1 mL)为分散剂, 24 种农药的检出限为 0.33~7.45 μg/L, 回收率为 72.4%~103%, 该方法成功应用于鱼塘投毒案件中 α-硫丹、β-硫丹和甲氰菊酯的检测。

2.2 蔬菜水果

蔬菜水果是农药残留的高风险食品, 开展蔬菜水果中农药残留分析对保障我国食品安全具有重要意义。由于 DLLME 技术只适用于液体样品, 在分析蔬菜水果等固体样品时需要对样品先进行预处理再进行 DLLME 操作。郭伟等[27]以三氯甲烷(50 μL)为萃取剂, 0.04 mmol/L 的 S-80 表面活性剂(0.5 mL)为分散剂, 采用表面活性剂辅助 DLLME 与 GC (gas chromatography)联用分析蔬菜水果中的 8 种有机磷农药, 8 种农药在 0.02~0.50 μg/mL 内具有良好的线性关系, 回收率 82.4%~114.5%之间, RSD 低于 13.7%。Wang 等[28]建立了 QuEChERS-DLLME-GC-MS 检测芹菜中 9 种农药残留的分析方法, 样品经 QuEChERS 方法处理后, 以三氯甲烷(100 μL)为萃取剂, 乙腈(800 μL)为分散剂, 涡旋 1.5 min, 9 种农药的回收率为 70.8%~93.2%, 检出限为 2.4~14.2 μg/kg。Pirsaheb 等[29]采用 SFOD (solidification of floating organic drop)-DLLME 与 HPLC(high performance liquid chromatography)联用同时测定苹果中阿维菌素、二嗪农和毒死蜱, 以 1-十一醇(30 μL)为萃取剂, 乙腈(1 mL)分散剂, 三种农药在 2~500 μg/kg 范围内相关系数大于 0.9955, 检出限为 0.7~2 μg/kg。

2.3 牛 奶

随着人们生活水平和保健意识的提升, 牛奶作为补钙的最佳途径之一备受欢迎。牛奶在食物营养链中处于较高级, 其含有的农药残留量相对较高, 因此监测牛奶中的农药残留十分必要。由于牛奶中存在较多的脂肪和蛋白质, 进行 DLLME 操作之前需先用有机溶剂提取, 把牛奶中的农药残留和杂质分离出来。Zhao 等[30]建立了 DLLME-GC-ECD 同时检测牛奶中 4 种六六六同分异构体和 6 种拟除虫菊酯农药残留的分析方法, 牛奶样品经乙腈提取和 PSA 净化后, 以低密度的环己烷(140 μL)为萃取剂, 乙腈(0.5 mL)为分散剂, 10 种农药检出限为 0.07~2 μg/kg, 回收率为 70.1%~106.3%。Farajzadeh 等[31]建立了 DLLME 和 GC-FID、GC-MS 分析牛奶中 5 种三唑类农药的分析方法, 样品用乙腈提取后, 以三氯甲烷(40 μL)为萃取剂, 乙

腈(1 mL)为分散剂, 5 种农药检出限为 4~58 μg/L, 富集倍数为 156~380。Gao 等[32]采用 DLLME-SFOD 与 GC-ECD 分析牛奶中 7 种拟除虫菊酯农药, 牛奶样品经乙腈提取后, 以低密度的正十六烷(30 μL)为萃取剂, 丙酮(800 μL)为分散剂, 氯化钠浓度为 6% (*w*/*w*), 7 种农药检出限为 0.08~0.44 μg/L, 回收率为 90.2%~108.4%, 将该方法与文献报道的其他 4 种方法相比, 具有回收率高、有机溶剂用量少等优点。

2.4　酒

酒主要是以谷物、水果、中药等原料酿制而成, 然而在酿酒原料种植过程中存在较为普遍的农药残留问题, 致使酿造的酒中仍可能有部分农药残留。目前 DLLME 主要应用于葡萄酒中农药残留的检测, 由于葡萄酒基质简单且酒精含量低, 葡萄酒样品无需任何处理即可直接进行 DLLME 操作。郭亚芸等[33]以超声辅助(ultrasound-assisted, UA)DLLME 为富集和净化手段, 采用 GC-MS 检测葡萄酒中戊菌唑等 4 种三唑类农药残留量, 以低密度的十一醇(30 μL)为萃取剂, 超声 10 min 后离心, 十一醇在液面成漂浮液珠, 冰浴液珠凝固后取出, 待溶化后进行 GC-MS 分析, 4 种农药检出限为 0.019~0.039 μg/L, 回收率为 7.3%~107.5%。徐豪等[34]建立了 DLLME-GC-MS/MS 分析葡萄酒中 12 种农药残留的方法, 以四氯化碳(30 μL)为萃取剂, 丙酮(0.8 mL)为分散剂, 12 种农药的富集倍数为 123~196, 检出限为 0.0006~0.0051 μg/L。Chu 等[35]建立了 UDSA(Up and down shaker assisted)-DLLME 和 GC-M 分析葡萄酒中嘧菌环胺、腐霉利等 6 种杀菌剂的方法, 以低密度的 1-辛醇 (11 μL)为萃取剂, 无需分散剂, 6 种杀菌剂的检测限为 0.007~0.025 μg/L, 富集因子为 480~1254, 通过和经典的 DLLME、USAEME 方法进行比较, 表明该方法有更好的富集效果。

2.5　蜂　蜜

蜂蜜因为其营养价值高且纯天然而受到人们的喜爱, 然而蜜源植物和蜜蜂体内的农药残留可能污染蜂蜜, 从而危害人体健康。王东等[36]建立了 DLLME 与 GC-MS 联用快速检测蜂蜜中六六六和滴滴涕类农药残留的分析方法, 以三氯甲烷为萃取剂(70 μL), 乙腈为分散剂(1.1 mL), 8 种农药的检出限为 20 μg/kg, 富集倍数为 74~96。Shirani 等[37]建立了固相萃取(solid phase extraction, SPE)-DLLME-GC-MS 同时分析蜂蜜中溴氰菊酯和氯菊酯残留量的方法, 以四氯化碳为萃取剂(30 μL), 甲醇为分散剂(1 mL), NaCl 浓度为 4% (*M*/*V*), 溴氰菊酯和氯菊酯的检出限分别为 0.04 ng/g 和 0.02 ng/g。Kujawski 等[38]建立了 DLLME-GC-MS 分析蜂蜜中 11 种有机氯农药残留量的方法, 以三氯甲烷为萃取剂(100 μL), 丙酮为分散剂(450 μL), 各农药的检出限为 0.1~4.0 ng/g, 将该方法用于波兰的 19 个蜂蜜样品的分析, 检出农药艾氏剂、异狄氏剂、林丹、4,4′-DDT。

2.6　粮　谷

为了保证粮谷产量和储藏安全, 在粮谷生产及储运过程中难以避免使用各种农药, 因此粮谷中农药残留问题是目前食品安全中的主要问题之一。由于粮谷基质成分复杂, 在粮谷农药残留的检测中 DLLME 经常与 QuEChERS、SPE 等前处理技术联用以保证测定结果的准确性。Cunha 等[39]建立了 QuEChERS-DLLME-GC-MS 检测玉米中 41 种农药残留的分析方法, 样品经 QuEChERS 方法提取净化后, 以四氯化碳(100 μL)为萃取剂, 乙腈(1 mL)为分散剂, 82%农药的回收率为 70%~120%, 63%农药的检出限低于 19 μg/kg。将该方法用于 10 个玉米样品的检测, 在 2 个玉米样品检出 5 种农药残留。Khalilian 等[40]建立了 UAE-SPE-DLLME 和 HPLC 联用检测大米中二嗪磷和毒死蜱的分析方法, 以氯苯为萃取剂(55 μL), 乙腈为分散剂(1.5 mL), 二嗪磷和毒死蜱的检出限分别为 1.5 μg/kg、0.7 μg/kg。Wang 等[41]建立了 DSPE-DLLME-HPLC 检测谷物(大米、玉米、小米、燕麦)中烯啶虫胺等 7 种新烟碱类杀虫剂的方法, 以 $CHCl_3$: CH_2Cl_2 (1:1, *V*/*V*) (2 mL)为萃取剂, 乙腈(1 mL)为分散剂, 7 种农药回收率为 76%~123%, 检出限为 0.002~0.005 mg/kg, 将该方法用于黑龙江、内蒙古、云南 3 个省份的 4 种谷物的测定, 共检出噻虫嗪、吡虫啉 2 种农药。

2.7　茶　叶

茶叶是我国传统养生保健品, 具有抗肿瘤、抗氧化、改善心血管疾病等一系列特殊保健功能, 深受人们的喜爱。由于茶叶种植过程中存在农药不合理使用及滥用等行为, 导致茶叶中存在严重农药残留问题。由于茶叶成分复杂, 目前 DLLME 在茶叶农药残留的检测中应用较少。高玉玲等[42]建立了 UA-DLLME-SFO-GC 测定茶叶中 5 种拟除虫菊酯残留的方法, 茶叶样品经乙腈提取后稀释, 以十六烷为萃取剂(20 μL), 丙酮为分散剂(800 μL), 氯化钠质量分数为 4%, 水相 pH 为 4, 5 种农药的检出限为 0.11~0.24 μg/kg, 与其他公开发表的 d-SPE-GC 等方法比较, 该方法操作更简便且灵敏度更高。孙梦园等[43]结合 d-SPE 净化技术和 DLLME 技术, 并与 GC-MS/MS 联用, 成功地应用于茶叶中 7 种拟除虫菊酯类农药残留的测定。以四氯化碳为萃取剂(200 μL), 乙腈为分散剂(1 mL), 萃取时间为 1 min, 回收率为 75.4%~113.6%, 定量限为 1.0~10.0 μg/kg。Li 等[44]建立了 QuEChERS-DLLME-GC-MS/MS 检测茶叶中 47 种农药残留的分析方法, 样品经 QuEChERS 方法处理后, 以四氯化碳(200 μL)为萃取剂, 乙腈(1 mL)为分散剂, 绿茶、乌龙茶、红茶、普洱茶中大部分农药的检出限小于 10.0 μg/kg, 回收率为 70%~120%。将该方法用于 24 个茶叶样品的检测, 共有 15 种农药在 21 个样品中检出。

2.8 中药材

中药作为中华民族的瑰宝，在人们的日常生活中发挥着重要的作用。目前 DLLME 已成功应用于人参、党参、金银花、枸杞、山药等中药材农药残留的检测中。Chen 等[45]建立了 QuEChERS-DLLME-UPLC-MS/MS(ultra performance liquid chromatography-tandem mass spectrometry)联用检测人参中 39 种农药残留的方法，人参样品经 QuEChERS 方法处理后，三氯甲烷(100 μL)为萃取剂，乙腈(1 mL)为分散剂，氯化钠浓度为 8%(*w/V*)，39 种农药相关系数均大于 0.99，检出限为 0.01~1.0 μg/kg。周卿等[46]将党参样品用正己烷超声提取后，以邻二氯苯(60 μL)为萃取剂，甲醇(200 μL)为分散剂，涡旋 30 s，建立了 DLLME 与 GC 快速测定党参中 10 种有机氯类农药残留的方法，10 种农药回收率为 90.1%~109%，检出限为 0.5~3.0 μg/kg。Wei 等[47]建立了 UA-DLLME 和胶束扫集电动色谱 (sweeping micellar electrokinetic chromatography, sweeping-MEKC)联用检测枸杞、山药、党参和人参中 9 种有机磷农药残留量的分析方法，三氯甲烷(350 μL)为萃取剂，丙酮(1 mL)为分散剂，氯化钠浓度为 6%(*m/V*)，该方法对 9 种农药的富集倍数为普通 MEKC 方法的 779.0~6203.5 倍，9 种农药的检出限为 0.002~0.008 mg/kg，相对标准偏差为 1.2%~6.5%。

2.9 土 壤

目前，施用于农田中的农药大部分进入土壤，残留在土壤中的农药会随着外界环境的变化而不断释放，经各种介质进入人体和动植物组织中，危害人类健康安全。由于土壤基质复杂，DLLME 在土壤中农药残留的检测常与传统的提取净化技术相结合，进一步通过 DLLME 富集提高方法的灵敏度。成昊等[48]建立了 MSPD(matrix solid phase dispersion)-DLLME -GC-MS 测定土壤中胺菊酯、氯菊酯、溴氰菊酯的分析方法，样品与固相萃取粉末研磨后以丙酮洗脱并浓缩后加入 20 μL 四氯化碳和 5 mL 超纯水形成乳化，离心破乳后吸取沉积相进 GC-MS 分析，3 种农药回收率为 86.5%~108%，检出限为 1.00~1.48 μg/kg。Wang 等[49]建立了 UA-DSPE-LDS(low-density solvent)-DLLME 和 GC-PFPD 联用检测土壤中 6 种有机磷农药残留的方法，土壤样品用丙酮提取后经 DSPE 净化，以 2-乙基己醇(100 μL)为萃取剂，丙酮(1 mL)为分散剂，6 种农药的检出限为 0.2~0.5 ng/g，相对标准偏差小于 8%，富集倍数为 22~35。Pastor-Belda 等[50]建立了 SLE(solid-liquid extraction)- DLLME-LC-MS/MS 检测土壤中氯虫苯甲酰胺等 5 种农药残留的方法，样品经乙腈提取后以四氯化碳(125 μL)为萃取剂，乙腈(1.5 mL)为分散剂，5 种农药定量限为 0.005~0.030 ng/g，和未经 DLLME 富集的 SLE-LC-MS/MS 方法(定量限为 0.1~0.5 ng/g)相比，该方法灵敏度更高。

2.10 生物样本

生物样本组成复杂且农药含量很低，在进行仪器分析之前，选用一种具有富集效果的样品前处理技术至关重要，DLLME 由于具有富集倍数高的优点，目前已成功的应用于生物样本的农药残留检测中。Li 等[51]建立了 UETC(ultrasound-enhanced temperature-controlled)-IL(ionic liquid)-DLLME-HPLC 分析老鼠血液中 5 种三唑类农药残留的方法，以[C_6MIM][PF_6](100 μL)为萃取剂，甲醇(200 μL)为分散剂，5 种农药的回收率为 88.9%~98.5%，富集倍数为 178~197，检出限为 4~6 μg/L。周信康等[52]建立了 DLLME 与 GC-MS 联用分析人体尿液中 3 种拟除虫菊酯类杀虫剂的方法，以低密度的薄荷醇为萃取剂，该萃取剂在低温下即可冷凝为固态浮在水相上层，可避免受生物杂质沉淀的干扰，且该萃取剂无毒无味，绿色环保。Jouyban 等[53]建立了 DLLME-GC-MS 检测农民尿液和血浆中二嗪农等 10 种农药残留的方法，该方法以 41 μL DES(薄荷醇:苯乙酸)为萃取剂，无需分散剂，10 种农药的回收率为 79%~97%，检出限为 2~17 ng/L(尿液)和 4~36 ng/L(血浆)，富集倍数为 379~485(尿液)和 158~194(血浆)。

3 结 论

DLLME 作为一种新型的液液微萃取技术，与其他的萃取技术相比，具有操作简便、快速、环境友好、富集倍数高等优点，近年来在农药残留的检测中得到广泛的应用。虽然 DLLME 对于基质复杂的样品选择性差，往往需要进一步的提取和净化才能取得满意的分析效果，但通过与其他净化或萃取技术相结合，拓宽了 DLLME 的应用范围，使其更适合于复杂样品中农药残留的分析。然而目前 DLLME 方法还存在一定的局限性，开发新型的萃取剂和分散剂、研发萃取装置实现自动化操作、与其他样品前处理技术相结合扩大样品适用范围，仍是 DLLME 技术今后发展的趋势。随着研究的不断深入，DLLME 在农药残留分析中将会有更加广阔的应用前景。

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