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食品中农药残留检测前处理技术进展

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摘要:样品前处理是检测食品中农药残留的关键部分,为提高食品中农药残留检测的准确度和精确度,各种农药残留检测前处理技术不断地出现,极大地提高了食品中农药残留检测的效率,综述了食品中农药残留检测的样品前处理技术。

关键词:食品安全; 农药残留检测; 前处理方法; 萃取; 净化
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A Review of Pretreatment Methods for Determination of Pesticide Residues in Food

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Abstract: Sample preparation is the key part of determination of pesticide residues in food. All kinds of pretreatment methods for the determination of pesticide residues in food keep popping up to improve the accuracy and precision of determination, and improve greatly the efficiency of the determation of pesticide residues in food. This paper summarizes the pretreatment methods for determination of pesticide residues in food.

Key words: food safety; determination of pesticide residues; pretreatment methods; extraction; purification

食品中农药残留检测一般包括以下四个步骤:萃取、净化、浓缩、色谱分析等,其中前3个步骤是样品的前处理过程。在样品分析中,前处理所需时间占整个分析时间的2/3,而且90%的误差都来源于样品的前处理过程。因此,选择一种简单、快速、高效、环境污染小的样品前处理方法已成为当今重要课题之一。我国是农药生产和使用大国,食品中农药残留可以导致急慢性农药中毒,引起神经功能紊乱[1],甚至可能威胁人民生命安全[2-4];同时国际农药残留限量标准作为技术壁垒影响了我国食品的进出口贸易,成为我国出口食品的主要制约因素。农药残留是痕量的,且存在农药同系物、异构体、降解产物、代谢产物、基质等的影响,要想除去与目标物同时存在的杂质,减少检测过程中的干扰峰,避免检测器和色谱柱污染,选择合适的前处理方法至关重要[5]。现在常用的食品中农药残留检测前处理方法有:固相萃取(SPE)、固相微萃取(SPME)、超临界流体萃取(SFE)、基质固相分散萃取(MSPD)和加速溶剂萃取(ASE)等,这些方法具有快速、微型、环境友好等优点。

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1　固相萃取法

固相萃取(solid phase extraction , SPE) 首次出现在 1970 年,它基于液 - 固色谱理论,利用固体吸附剂将液体样品中的目标化合物吸附,与样品的基质和干扰化合物分离,再利用洗脱液洗脱(也可选择吸附干扰杂质) ,实现组份分离净化,现已经成为绿叶蔬菜、水果、乳品中农药残留检测前处理的基本方法[6] 。但目前该方法仍然存在以下不足: 一是处理复杂样品时,有时会引起回收率的偏低,对目标物有吸附作用; 二是吸附剂选择性不强,提取液净化不完全,不能吸附某些基质,造成检测的基质效应明显。Yang 等[7] 先将浆果样品用乙腈萃取,离心后吹干,再用乙腈 - 甲苯溶解,依次用 Envi - Carb 固相萃取柱和 NH_2 - LC 固相萃取柱净化,最后用 GC - MS 检测。回收率在 63% ~137%,相关系数 $R^2 > 0.99$。Satpathy 等[8] 检测了蔬菜和水果中多种农药残留,使用了微波辅助萃取和分散固相萃取,方法具有快速、高效、环境友好等优点,检出限为 0.002 ~0.02 mg/kg,定量限为 0.025 ~0.100 mg/kg,回收率是 72% ~114%,相对标准偏差 $RSD < 20\%$。分散固相萃取操作是: 2 mL 提取液加入到装有 PSA 和 $MgSO_4$ 混合物的离心管中,混匀之后离心,取 1 mL 上清液蒸干,溶于乙酸乙酯中用 GC - MS 检测。Oellig 等[9] 用高通量二维固相萃取法处理苹果、红葡萄、土豆等样品,避免了干扰物和基质的影响,LC - MS 检测发现回收率在 90% ~104% ,相对标准偏差为 0.3% ~4.1%,处理一个样品只需要几分钟,并且降低了样品和溶剂的需要量。

2　固相微萃取法

固相微萃取法(solid phase microextraction,SpME) 不需溶剂,通过萃取头涂液对目标物进行吸附、解吸、分析,集萃取、纯化、浓缩为一体,解决了传统固相萃取的一些缺点,如油性物质或固体对吸附剂的堵塞等,同时缩短了分析时间,二次污染微小,广泛用于挥发性、半挥发性物质的富集和检测,包括在粮食、蔬菜、水果、饮料等各类食品中的应用[10 - 11] 。固相微萃取与固相萃取的不同之处在于微型化,首先将涂有聚合物的石英玻璃纤维放入样品溶液中,之后再把石英纤维置于检测仪器之上,在那里分析物解吸、分离、定量检测[12] 。固相微萃取可以分为顶空和直接浸入[13] 两种类型。顶空法可以避免基质的影响[14 - 15] ,具有简便、快速、高效率的优点[16] 。但该方法纤维萃取针头寿命短,纤维上吸附一些杂质以后,难以清除,对结果的准确性有一定的影响,自动化程度低、目标化合物的回收率和精密度都低于液 - 液萃取。Rodrigues 等[17] 利用顶空固相微萃取法提取了牛奶中有机磷农药残留,并对固相微萃取的条件进行了优化。采用 PDMS - DVB 纤维头对样品进行顶空吸附,萃取温度 90 ℃,萃取时间 45 min,平衡时间 30 min,解析时间 5 min,搅拌速度 300 r/min,最后采用 GC - MS 检测。Melo 等[18] 利用高效液相法(二级阵列管检测器) 测定了生菜中多种杀虫剂残留,采用固相微萃取法处理样品。分别试验了 4 种萃取涂层: PDMS (100 μm) 、PDMS/DVB (60 μm) 、CW/TPR (50 μm) 、PA(85 μm) 的萃取效果,并对萃取温度、萃取时间等条件进行了优化。最后发现将 CW/TPR 萃取纤维直接侵入到样品溶液中,室温下萃取 30 min,萃取时以 1 000 r/min 的速度不断搅拌,萃取效果最好。Kin 等[19] 测定了清洗过的黄瓜和草莓中的农药残留,样品采用顶空固相微萃取法进行了前处理。将粉碎的样品准确称量 30 g 置于烧杯中,加入 30 g 蒸馏水,混匀之后加入到分离瓶中,再加入甲醇/丙酮混合溶剂(1∶1) ,最后将含 100 g/L NaCl 的蒸馏水将缓慢加入,直到瓶内样品的质量共是 5 g,PDMS 纤维头顶空萃取之后用 GC - ECD 检测。

3　基质固相分散萃取法

基质固相分散萃取(matrixsolid - phase dispersion extraction,MSPD) 集传统的样品前处理中的均化、提取、净化等过程为一体,避免了样品均化、沉淀、离心、转溶、乳化、浓缩等造成的目标分析物的损失,具有简便、灵活、快速、低耗等优点[20] ,已被广泛应用于药物[21 - 22] 、农药[23 - 24] 、食品[25 - 26] 、动植物样品[27 - 29] 的分析。1989 年美国 Barker 等首次提出可同时分散与萃取固体、半固体样品的基质固相分散萃取技术,该技术减少了组织匀浆、沉淀、离心、pH 调节和样品转移等操作,避免了样品的损失,并逐渐在各个领域得到广泛应用,其实质是基质分散固相萃取。2003 年 Anastassiades 等[30] 开发出一种快速(quick) 、简单(easy) 、廉价(cheap) 、高效(effective) 、耐用(rugged) 、安全(safe) 的样品前处理方法

(QuEChERS),2007 年 Lehotay 等[31] 对该方法进行了改进。目前该方法已发展成一系列针对不同基质的方法,是一种发展潜力很大的处理方法,也是目前水果、蔬菜等产品农药残留检测最常见的前处理方法。Chen 等[32] 开发了一种测定茶叶中多种农药残留的方法,样品前处理使用了 QuEChERS 法。即乙腈提取,提取液经离心后,用固相萃取柱净化,去除离心提取液中的干扰基质,然后直接进行在线 UP-LC/MS/MS 分析。回收率在 70% ~120%,RSD 符合欧洲质量规范。Stephen 等[33] 用高效液相色谱 - 质谱/质谱法测定了鸡蛋、奶酪、巧克力、咖啡等多种食品中痕迹量级有机磷和氨基甲酸酯类农药残留,样品前处理采用 QuEChERS 法。样品用高速混合机混合之后,取出 10 g 样品加入到装有硫酸镁、乙酸钠、氯化钠的具塞离心管中,再在离心管中加入 14 mL 含有 1% 乙酸的 CH_3OH,剧烈振荡之后,以 8 500 r/min 转速离心 5 min,净化、就完成了样品的前处理。

4 液液微萃取法

液相微萃取(liquid liquid microextraction, LLME) 是 20 世纪 90 年代发展起来的一种操作简单、高效的萃取技术[34-37],在食品安全领域常被用来处理水分含量比较大的水果、酒类等,最初是在 1996 年由 Liu[38] 和 Jeannot[39] 开创的。和传统的液液萃取相比是一种成本低、有机溶剂用量少、环境友好的样品前处理新技术,在食品安全领域得到了广泛的应用[40-41]。液相微萃取可同时平行萃取多个样品,且净化效率高。1996 年 Jeannot 等[39] 首次研究了顶空液相微萃取法,适用于容易进入样品上方空间的挥发性或半挥发性有机化合物的分析测定,应用范围受到了很大的限制。再到后来由 Pedersen - bjergaard 等[42] 首次提出了中空纤维液相微萃取法,中空纤维液相微萃取的原理与传统的液相萃取相同。Li[43] 利用中空纤维液相微萃取提取了鲜葡萄中的多种农药残留,萃取和净化用 SiO_2 中空纤维一步完成。将 SiO_2 中空纤维浸泡在 1 mL 加标的葡萄液中,一定时间后取出,放入盛有乙酸乙酯的离心管中,在超声条件下,待检物被提取到溶液里面,提取液用 GC - MS 检测,用去离子水和纯乙醇冲洗提取纤维后就可以重复利用,提取效率没有任何降低,回收率在 61% ~108%,相对标准偏差 4.0% ~12.4%,该方法具有准确度高、重复性好等优点。Sun 等[44] 将食用鱼样品经过均质、冷却、超声辅助萃取、离心、蒸发浓缩之后,进行中空纤维液相微萃取。PVDF 纤维萃取头安装在切除了一部分的移液管上,再用微量注射器将 30 uL 邻二甲苯注入到萃取头中,再将它置于先前的溶液中萃取 30 min,搅拌速度是 500 r/min。最近 Rezaee 等[45] 又报道了分散液液微萃取技术,该方法具有操作简单、快速、成本低、对环境友好且富集效率高[46-47] 等优点,适用于亲脂性高或中等的食品的分析,在食品中农药残留检测等痕量分析领域具有广泛的应用前景[48-50]。Farajzadeh 等[51] 采用分散液液微萃取法提取了果汁和水果中 3 种有机磷农药含量,用氯仿和甲醇分别作分散溶剂和萃取溶剂,回收率可以接近 100%。该方法的缺点是选择性差,难以用于复杂基质样品,可能使用毒性较大的卤代烃做萃取剂,取出沉降于试管底部的萃取剂存在一定的操作难度。

5 凝胶渗透色谱法

凝胶渗透色谱法(gel permeation chromatography, GPC) 最早是在 1972 年由 Stalling 等[52] 提出,该方法利用多孔物质依据不同组份的分子大小和形状不同进行分离、萃取和净化,特别适用于将小分子化合物从大分子化合物中分离出来。优点是使用范围广、重现性好、可以重复利用柱子以及自动化程度高,适用于多类食品提取液的净化,尤其对脂类和色素含量高的食品样品净化效果明显。已经逐渐成为除去食品中脂肪等必用的方法[53]。主要缺点是大分子的分析物会随着脂类干扰物提前流出,而小分子的干扰物会夹带洗脱到分析物中,回收率受到影响; 采用大内径柱时,有机溶剂消耗量大,净化时间长。Lu 等[54] 检测了蔬菜和水果中 45 种农药残留,样品经过盐析和相分离两步,再用在线凝胶色谱法除去基质效应的影响,极大地提高了方法的灵敏度和回收率。Yu[55] 通过 GPC - GC/MS 研究了 176 种农药残留检测中基质效应的影响。农药的基质效应可以减弱或增强检测仪器的信号,造成误差,而通过在线凝胶色谱技术、大体积进样技术和程序化升温模式可以有效控制基质的影响。

6　其它前处理方法

6.1　超临界流体萃取法

超临界流体萃取(supercritical fluid extraction, SFE) 是一种效率高、时间短、溶剂消耗少的萃取技术[56]。主要原理是利用超临界流体中不同组分溶解度不同,且不同压力下同一组分溶解能力不同,改变萃取剂流体压力,可将组分逐一萃取分离。最常用的超临界流体是 CO_2,可用于提取非极性或极性较小的农药。该方法的优点是具有很好的萃取效力和速度,与分析仪器在线联机,大大地提高了灵敏度;缺点是仪器设备昂贵,实验成本高,且萃取过程中需要优化较多参数,且不同样品的分析都要重新优化参数,样品基质对萃取结果影响较大。El - Saeid 等[57] 检测了沙特阿拉伯利雅得地区 8 个市场上的 Khalas, Sukkari, Nabout Seif 等 3 种水果中的杀虫剂、除草剂等的残留,样品前处理分别使用了超临界流体萃取和微波振荡提取。超临界流体萃取第一步中,CO_2 密度为 0.25 g/mL,萃取压力 77 bars (1 117 psi),温度 40 ℃,CO_2 流速 1.0 mL/min; 第二步中 CO_2 密度是 0.67 g/mL, 萃取压力 239 bars (3 469 psi),温度 80 ℃,CO_2 流速 2.5 mL/min。

6.2　加速溶剂萃取法

加速溶剂萃取(accelerated solvent extraction, ASE) 根据分子印迹聚合物的特殊优点,将其用做固相萃取的吸附剂材料,具有较高的特异性和选择性,对模板分子有预定的识别性而且制备方法简单。具有溶剂用量少、萃取时间短、萃取效率高等优点,是一种绿色环保的新型萃取技术[58],在食品安全检测等诸多领域[59-60]逐渐得到应用。Wua 等[61] 开发了一种分析食品中多农药残留的新方法,样品先采用加速溶剂萃取法萃取,之后再用凝胶渗透色谱法除去里面的脂肪和其它的基质影响物。具体做法是: 将一定量的鸡肉、鱼肉等样品置于研钵中研细混匀脱水,进行加速溶剂萃取,萃取温度 80 ℃,萃取压力 1 500 psi (10.3 MPa),加热时间 5 min,静态萃取 5 min,再用样品体积 60% 的乙腈冲洗,最后用氮气净化,就完成了萃取过程。Zhang 等[62] 建立了一种加速溶剂萃取法萃取、固相萃取法净化,再用 GC - ECD 分离分析谷物类作物中 14 种有机氯残留的方法。比较了 ASE、HSHE、和 SE 等 3 种萃取方法的效率,最后发现 ASE 方法最优。采用 ASE 萃取大多数样品回收率在 80% ~115%,加标回收率在高低两个水平分别为 83.9% ~115.8% 和 78.9% ~111.9%,相对标准偏差在两个水平分别是 1.8% ~16.4 % 和 1.1% ~10.3%。

6.3　微波辅助萃取法

微波辅助萃取(microwaveassisted extraction, MAE) 也是一种农药残留萃取中常用的方法。微波搅拌使固 - 液更密切接触, 加速了分析物的溶解和扩散, 提高了提取效率。利用微波给萃取溶剂提供能量产生局部的高温高压,使目标分析物很快的从基质转移到萃取液里面[63]。1986 年 Ganzler 等[64] 首先报道了微波用于天然产物成分的提取,现在此项技术已广泛应用于食品、生物样品及环境样品的分析与提取[65-66]。Qu 等[67] 检测了韭菜中有机磷农药残留,样品前处理中使用了微波辅助萃取。将 3.0 g 切碎的韭菜样品放入一个 50 mL 离心管,在 640 W 功率下,微波加热 10 s,然后在冰水浴中迅速冷却。再将 3 mL 色谱纯水和 15 mL 含有 1 g/L 醋酸的乙腈加入离心管中,涡旋均质仪 9 000 r/min 的转速混匀。这样有机磷农药就被初步萃取到了溶液当中,而且除去了样品中蒜氨酸酶对结果的影响。Karmakar 等[68] 用水作为萃取溶剂,微波辅助萃取了蔬菜中的噻虫嗪残留,HPLC 进行了检测。将 10 g 样品放置于 100 mL 烧杯中,注入 40 mL 去离子水,用表面皿盖住烧杯放入微波炉中,在 500 W 功率下,加热 30 s,之后放到冰箱里面冷却,再重新微波加热,最后再经过离心、SPE 萃取净化。与传统的混合器和索氏提取法相比,微波辅助萃取法具有较高的精确度($RSD < 3\%$)。

6.4　超声波萃取法

超声波萃取(ultrasonic extraction, UE) 是基于超声波的特殊物理性质,利用超声过程中产生的快速机械振动波来减小目标萃取物与样品基体之间的作用力,实现快速萃取,常常作为一种辅助方法,在肉类、谷物等检测中有着广泛应用。Bidari 等[69] 将番茄样品切碎之后,通过超声波萃取,萃取之后不需要净化和蒸发。具体做法是: 将切碎混匀的样品准确称量之后置于具塞离心管中,加入丙酮,再将离心管置于超声波清洗器中 35 min,就完成了超声波辅助萃取。该方法简单、经济,适用于露天农田种植番茄

中有机磷农药残留的检测。Deng 等[60]分析了苹果中己唑醇、腈菌唑、戊唑醇等 3 种农药残留，在处理土壤样品时采用了超声波萃取。将过筛的样品溶于 60 mL 1∶1 (*V*/*V*) 的甲醇－水溶液，超声 30 min，再用二氯甲烷萃取 3 次，每次用 20 mL，合到一起的二氯甲烷萃取物在浓缩之前进行干燥。整个方法的回收率在 94.5% ~107.3%，灵敏性高 (0.01 mg/kg)，精密度好(RSD <9.7%)。

7 展 望

随着近年来在食品行业出现的越来越多的农药残留问题，以及由此而引发的人体健康、贸易壁垒、环境污染等诸多问题，使人们对食品中农药残留问题越来越重视，各种新型的农药残留检测方法不断出现，主要体现在新的前处理手段和新的分析仪器上，毫无疑问前处理方法是至关重要的一步。传统的食品中农药残留提取方法样品需要量大、萃取时间长、有机溶剂量消耗大、花费大、无法满足快速、准确的分析要求。二三十年来，许多新型前处理方法快速发展，极大地提高了农药残留检测的效率。展望以后食品中农药残留前处理技术将会继续朝着以下 3 个方向发展：1. 新方法将用较少的时间完成样品的处理；2. 样品处理仪器设备集成化、一体化、占用体积少，方便携带使用，各种新型微萃取装置将会得到进一步发展；3. 处理的结果具有高精确性和高准确性。

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