

农产品中新烟碱类农药残留快速检测技术研究进展

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摘要: 新烟碱类农药(neonicotinoid pesticides, NEOs)凭借高效、广谱、低毒和低残留等优势,在全球农业生产中得到广泛应用。但该类农药若被不当使用,会对生态环境造成污染,同时对人类健康构成严重威胁。因此,研发具备现场适用性、高通量特征的新型快速检测技术已成为当前的研究焦点。作者综述了NEOs残留快速检测技术的检测原理、优势与局限性,详细介绍了酶联免疫吸附测定、荧光免疫分析、免疫层析、表面等离子体共振(SPR)、表面增强拉曼散射(SERS)、荧光共振能量转移(FRET)、分子印迹技术(MIT)、金属有机框架材料(MOTs)和纳米材料电化学传感器等在农产品中NEOs残留检测中的研究进展。以免疫分析、光学分析、电化学分析为代表的农药残留检测技术凭借其高灵敏性、高选择性等优点,在痕量NEOs残留的快速检测中展现出巨大应用潜力,但在检测限降低、灵敏度提升和基质干扰消除等方面仍存在不足。未来在实际检测应用中,应重点围绕消除基质效应、实现智能化和自动化、推进多功能集成等方向进行创新与优化。

关键词: 新烟碱类农药; 农药残留; 免疫分析; 光学分析; 电化学分析; 快速检测

Research Progress in Rapid Detection Technologies of Neonicotinoid Pesticide Residues in Agricultural Products

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Abstract: Neonicotinoid pesticides (NEOs) are widely used in global agricultural production because of their high efficiency, broad spectra, low toxicity, and low residues. However, improper use of NEOs will cause environmental pollution and pose a serious threat to human health. Therefore, developing new rapid detection technologies with field applicability and high throughput has become the focus of current research. The author reviewed the principles, advantages, and limitations of rapid detection technologies of neonicotinoid pesticide residues, and introduced in detail enzyme-linked immunosorbent assay, fluorescence immunoassay, immunochromatography, surface plasma resonance (SPR), surface-enhanced Raman scattering (SERS), fluorescence resonance energy transfer (FRET), molecular imprinting (MIT), and electrochemical sensors based on metal-organic frameworks (MOTs) and nanomaterials in the detection of neonicotinoid pesticide residues in agricultural products. With high sensitivity and high selectivity, the pesticide residue detection technologies

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represented by immunoassay, optical analysis, and electrochemical detection demonstrate great potential for the rapid detection of trace neonicotinoid pesticide residues, while they still have certain limitations in terms of detection limits, sensitivity, matrix treatment, etc. In the future practical testing, attention should be paid to the innovation and optimization in matrix effect elimination, intelligence and automation, and multi-functional integration.

Keywords: neonicotinoid pesticide; pesticide residue; immunoassay; optical analysis; electrochemical analysis; rapid detection

NEOs是继有机磷、氨基甲酸酯和拟除虫菊酯类杀虫剂之后的第4类农药^[1-3],其作用机制为与昆虫中枢神经系统烟碱型乙酰胆碱受体(nAChRs)特异性结合,阻断神经信号传导,最终导致昆虫死亡^[2,4-6]。NEOs对哺乳动物的淋巴细胞具有基因毒性和细胞毒性^[3];此外,NEOs还对蜜蜂及蚯蚓等土壤无脊椎动物具有致命或亚致死作用^[5-8]。NEOs凭借高效、广谱、内吸性强及对哺乳动物低毒等特点,迅速占据全球杀虫剂市场的主导地位^[9]。截至2021

年9月,我国已登记的NEOs共12种,分别为吡虫啉(imidacloprid, IMI)、啉虫脒(acetamiprid, ACE)、氯噻啉(imidaclothiz, IMZ)、噻虫胺(clothianidin, CLO)、噻虫啉(thiacloprid, THD)、噻虫嗪(thiamethoxam, THM)、呋虫胺(dinotefuran, DIN)、啾虫啉(paichongding, PAI)、烯啶虫胺(nitenpyram, NIT)、环氧虫啉(cycloxaprid, CYC)、氟啶虫胺胍(sulfoxaflo, SU)和氟吡呋喃酮(flupyradifurone, FLU)^[5]。常见NEOs的化学结构见图1。

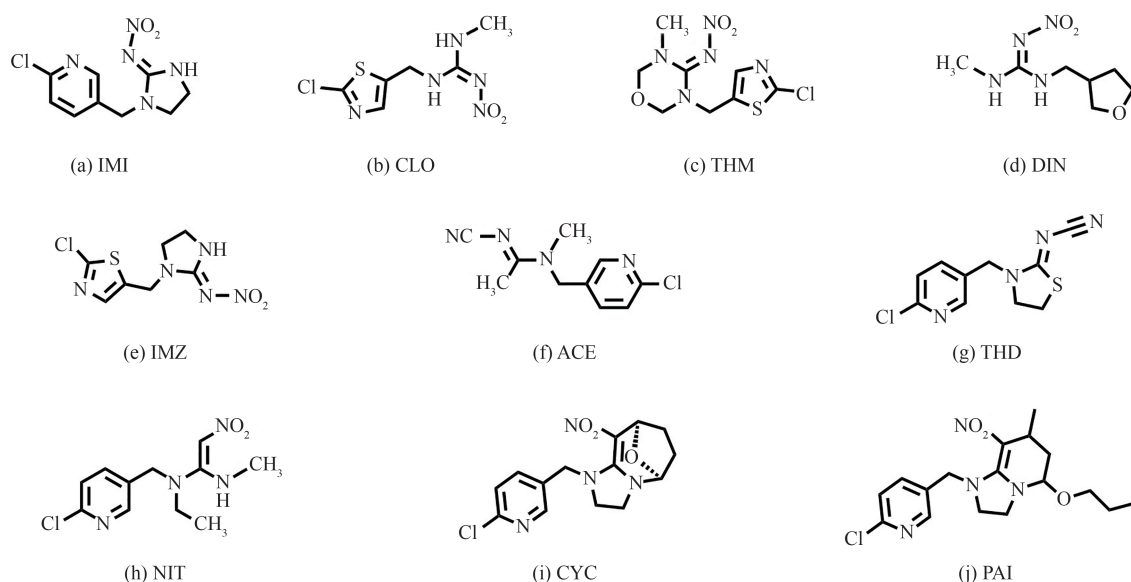


图1 NEOs的化学结构

Fig. 1 Chemical structures of NEOs

NEOs曾被认定为环境友好型农药,但由于其成本低廉、易引发害虫耐药性,导致滥用风险急剧升高^[10]。该类农药因其水溶性强、持久性高等特点,可在环境中广泛积累并沿食物链富集,不仅会造成生态污染,还会对人体健康构成严重威胁。例如,IMI和THM可通过抑制哺乳动物中枢神经系统的nAChRs干扰神经信号传导,引发头痛、震颤等神经症状,甚至可能对儿童神经发

育造成不可逆损害。此外,部分NEOs具有内分泌干扰特性,可能影响甲状腺激素平衡及生殖功能。有研究表明,该类农药暴露与精子质量下降、胚胎畸形率升高密切相关。目前欧盟虽已禁止部分NEOs使用,但多数国家仍因其经济优势导致监管政策存在显著差异。同时,NEOs代谢产物的毒性可能比母体化合物更高,但其毒理安全性、长期低剂量暴露的生态阈值尚未明确,导

致农业生产需求与生态环境保护之间难以形成有效的平衡。

综上所述,基于NEOs带来的环境风险、健康危害及现有的检测技术存在的瓶颈,研发高效、精准的NEOs残留快速检测技术成为保障农产品安全与人类健康的迫切需求。传统检测技术虽然精确度较高,但存在检测周期长、检测成本高等缺陷,难以满足复杂基质中痕量NEOs残留的现场快速检测需求,因此需开发更具优势的新型NEOs残留检测技术。作者系统综述了近年来NEOs残留检测技术的研究进展,以期应对相关环境污染与健康威胁、保障食品安全及指导农药合理施用提供科学依据。

1 NEOs残留快速检测技术

全球农业领域广泛使用的NEOs给生态环境和人体健康带来了潜在风险,而传统检测方法多依赖大型仪器,普遍存在样品前处理复杂、操作烦琐、耗时长等缺陷^[1,11-14]。高效液相色谱-质谱联用技术(HPLC-MS/MS)虽然灵敏度较高^[9],但仪

器购置成本高且需专业人员操作,难以满足现场快速检测的需求。近年来,光学分析、电化学分析及免疫分析等检测技术^[1]凭借高灵敏性、高选择性、操作简便等优势,已被广泛应用于果蔬、谷物等农产品的实时监测中。

1.1 免疫分析

免疫分析基于抗原与抗体的特异性结合实现农药的定性或定量检测^[15],常用技术包括酶联免疫吸附试验(enzyme-linked immunosorbent assay, ELISA)、荧光免疫分析(fluorescence immunoassay, FIA)及免疫层析(immunochromatography assay, ICA)等^[15],适用于复杂基质中农药残留的高通量筛查。

1.1.1 ELISA 技术

ELISA依托抗原抗体特异性结合与酶催化底物显色反应完成目标物的检测,主要分为直接竞争法和间接竞争法^[16-17]。该技术具有灵敏度高、操作简便、检测通量大等优势^[18],被广泛应用于食品安全检测与环境监测中^[19]。ELISA工作原理见图2。

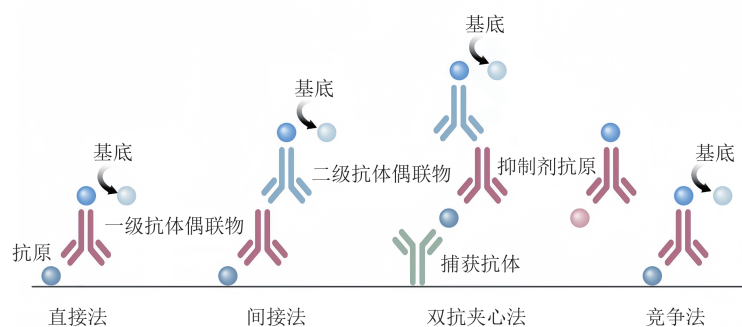


图2 ELISA工作原理

Fig. 2 Working principle of ELISA

间接ELISA主要用于蛋白质、细胞表面抗原等高相对分子质量抗原的定量检测^[17]。Watanabe等^[20]采用ELISA法检测稻米中的DIN,检测限低至0.6 ng/mL,回收率为92.5%~113.2%,检测结果与HPLC法高度一致。Li等^[21]构建了基于双酶示踪剂的多残留直接竞争ELISA体系,可实现THD和IMI的同步检测,在半数抑制质量浓度(IC₅₀)下的检测限分别为4.25、58.17 μg/L,且能有效减弱番茄、梨等样品中的基质干扰效应。然而,ELISA法仍存在抗体易发生交叉反应、批次稳定性不佳等问题,有待进一步优化以提升检测结果的可靠性。

1.1.2 FIA 技术

FIA通过荧光标记的抗体或抗原与目标物特异性结合后产生的荧光信号变化,实现对目标物的定性与定量检测。FIA工作原理见图3。

NEOs残留检测的样品前处理耗时较长,而时间分辨荧光免疫测定(TRFIA)可以显著缩短样品前处理时间并降低成本。Sheng等^[22]建立的双标记TRFIA技术,可同步定量检测食品基质中的CLO与烯唑醇,检测限分别为0.021 3、0.029 0 μg/L。Xu等^[23]开发出一种高灵敏度荧光免疫层析试纸条,用于果蔬中THD的检测,检测限低至

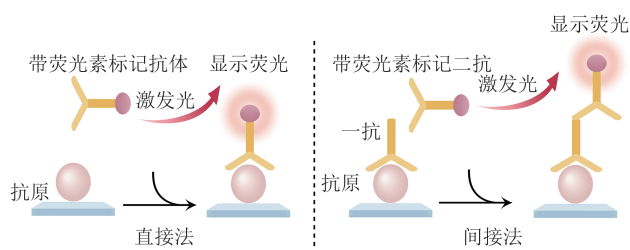


图 3 FIA 工作原理

Fig. 3 Working principle of FIA

0.003 ng/mL。此外,无机量子点(QDs)与链霉亲和素也被广泛应用于提升NEOs残留检测方法的灵敏度和稳定性。如Zhang等^[24]构建了基于QDs-链霉亲和素偶联物的FIA技术并用于IMI的检测,该技术大幅提升了检测灵敏度。Li等^[25]基于TRFIA体系构建了新型可交联荧光探针,用于蔬菜样品中ACE的检测,检测限低至0.62 ng/mL,线性检测范围为5~700 ng/mL,检测准确性较高。

研究证实,FIA比ELISA具有更高的灵敏度,但检测过程中易产生荧光猝灭现象,可能导致检测结果出现偏差^[17]。

1.1.3 ICA 技术

ICA技术是一种融合免疫胶体金技术与抗原、抗体特异性结合反应的农药残留快速检测方法,广泛应用于果蔬样品中NEOs残留的定性或半定量检测^[9,26]。ICA通常以抗体、抗原、酶等作为识别元件,但此类识别元件易受温度、酸碱度等环境因素的影响,抗干扰能力较差。ICA检测原理见图4。

ICA具有灵敏度高、特异性强和检测周期短等优势,可满足农业生产与食品安全监管中快速

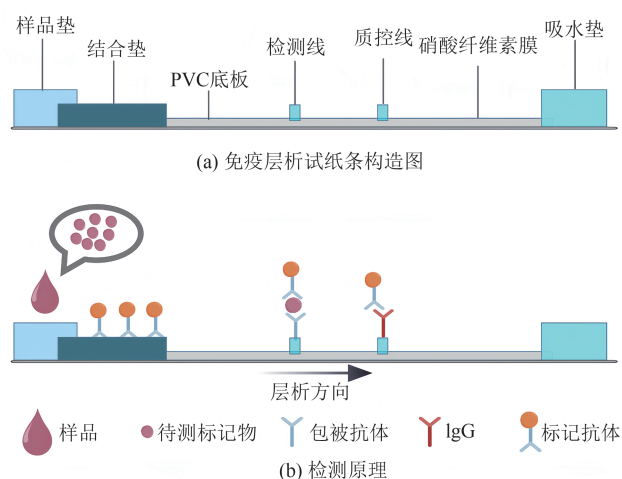


图 4 ICA 检测原理

Fig. 4 Detection principle of ICA

检测的需求。Tan等^[27]基于抗IMI单克隆抗体分别开发了胶体金侧向免疫层析法与时间分辨荧光纳米珠示踪侧流免疫层析法,用于IMI的定量检测;结果表明,2种方法检测限相近,对韭菜中IMI残留的分析结果一致性较好。此外,Cao等^[28]基于QD编码的多色微珠(QB),开发出多重免疫层析试纸条,可在单张试纸条上实现IMI、CLO、THM等多种NEOs的同步检测,且检测结果稳定性较好。QB反应速度快、操作简便,常作为金纳米颗粒(AuNPs)的理想替代材料。研究表明,AuNPs易与抗体偶联,常被用作光敏剂;纳米材料凭借其高生物相容性、结构可设计性及高信号输出能力,常被用作信号示踪器^[29]。据此,Sheng等^[30]以MoS₂@Au纳米复合材料作为信号载体和光热源,构建了一种结合色谱和光热效应的双模式ICA检测方法,并将其应用于IMI的快速半定量检测,实现了视觉和光热信号的同步输出与检测。

1.2 光学分析

光学分析法基于物质对光的吸收或发射特性,通过待测样品对特定波长光的吸收或发射行为来识别目标物,进而实现目标物的检测。近年来,基于SPR、SERS和FRET等多种光学传感器已用于农产品中NEOs残留的检测^[9]。

1.2.1 SPR 光学传感器

SPR光学传感器基于电磁波与物质的相互作用,通过实时分析分子相互作用,对固定在传感芯片上的目标组分进行定量检测。SPR光学传感器的检测原理见图5。

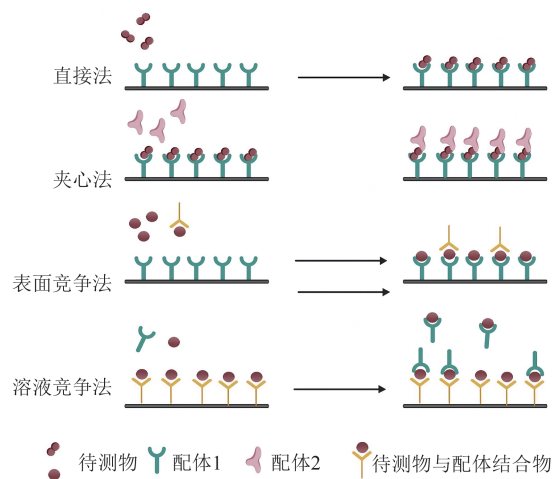


图 5 SPR 光学传感器检测原理

Fig. 5 Detection principle of SPR optical sensor

研究表明,结合了新烟碱类特异性气味结合蛋白2(OBP2A)的传感器可实现多种NEOs的同步检测^[31]。该蛋白质通过与AuNPs结合,能够隔离或掩盖杀虫剂的毒性,从而降低农作物对NEOs的敏感性。Wei等^[32]基于局部等离子体共振(LSPR)构建了更具实用性与快速性的农药检测系统,通过将OBP2A与数字纳米等离子体测定法相结合,显著提升了检测信噪比;结果显示,该系统对IMI、ACE和DIN的检测限分别为1.4、1.5、4.5 $\mu\text{g/L}$ 。相比之下,MIT虽能特异性识别目标物,但存在灵敏度低、操作复杂等缺陷。Ding等^[33]开发出寡肽功能化SPR生物传感器,实现了THD和IMI的实时快速检测,检测限分别为1.2、0.9 $\mu\text{mol/L}$ 。Wang等^[34]建立了荧光与LSPR技术相结合的双读出传感器法,可实现ACE与有机磷农药的同步检测及可视化分析。此外,虽然SERS技术的灵敏度较高,但其对结构相似的农药选择性较差,需结合化学计量学方法加以改善。

1.2.2 SERS 光学传感器

SERS光学传感器基于纳米粒子在介质中产生的SERS效应,可显著增强目标分子的拉曼信号,将检测限提升至单分子水平^[35]。该技术因具有灵敏度高、响应速度快、样品无需复杂前处理等优势,可作为NEOs残留的快速检测方法^[36]。

为进一步提高SERS的检测灵敏度,有研究开发出超疏水SERS基底,通过富集靶标分子实现目标物的高效检测。Gao等^[11]开发了一种光热诱导局部莱顿弗罗斯特的超疏水SERS传感器,不仅有效增强了SERS信号强度,还进一步降低了检测限。金属等离子体与半导体纳米复合可增强传感器敏感性,进而提升整体传感性能。如Thirumalairajan等^[12]以Ag/WO₃纳米纺锤体微球为柔性底物,开发出SERS传感器并应用于葡萄皮表面的IMI残留检测,检测限为10~11 mol/L 。此外,将SPR、SERS技术与化学计量学方法联用,可进一步提高检测方法的灵敏度与重复性^[36]。

近年来,各向异性金属纳米颗粒的可控制备已成为研究热点。如Abu Bakar等^[37]以银纳米颗粒(AgNPs)星型薄膜为SERS基底,可显著增强IMI检测的SERS信号,该基底具有高强度因子和低检测限。鉴于共振瑞利散射(RRS)与吸收光谱法具有操作简单且成本低的优势,Bai等^[38]构建了

一种三模传感器平台,该平台集SERS、RRS和吸收光谱3种传感模式于一体,有效避免了单一检测模式的不足。Cao等^[39]基于磁性分子印迹聚合物(MMIPs)构建了SERS系统,可快速测定农产品中ACE和THD的残留量。研究表明,MMIPs对目标物具备优异的磁分离富集性能,且该方法中复杂基质中靶标的提取与吸附时间极短,在NEOs的快速分析领域展现出良好的应用前景。

1.2.3 FRET 光学传感器

FRET光学传感器是指能量通过分子间或分子内的偶极-偶极相互作用,从而激发供体荧光团转移至受体荧光团的现象^[40],其作用机制见图6。这类传感器无需复杂的样品前处理和固定化步骤,大幅简化了NEOs的检测过程。

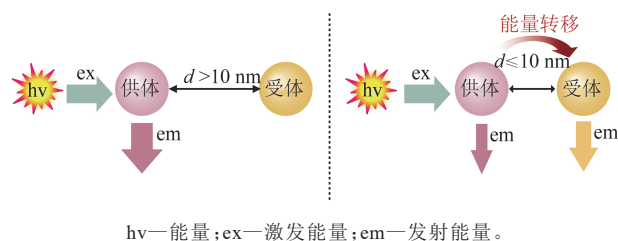


图6 FRET光学传感器作用机制

Fig. 6 Detection mechanism of FRET optical sensor

目前常用的荧光传感模式包括荧光增强、荧光猝灭和比率荧光3种^[41]。荧光传感器可通过荧光增强来响应目标物。Hu等^[42]制备了一种新型的适配体纳米传感器,实现了对ACE的定量检测,检测限低至3.2 nmol/L 。此外,基于FRET的传感器可通过荧光猝灭效应提升检测灵敏度。Guo等^[43]基于上转换纳米颗粒(upconverting nanoparticles, UCNPs)和氧化石墨烯(GO)构建了一种FRET免疫测定法,用于食品中IMI残留检测,线性检测范围为0.08~50.00 ng/mL 。

QDs作为一种新型的FRET试剂,凭借独特的光学特性和电子特性,可作为性能优良的FRET供体或受体。Luo等^[44]采用水热法制备了由石墨烯(GN)和碳点构成的FRET系统,由于IMI可有效猝灭该系统中碳点的荧光发射,因此可通过荧光强度变化实现对IMI的定量检测。Fang等^[45]以 β -环糊精(β -CD)修饰的螺吡喃为信号报告单元,合成了NH₂-SiO₂@CsPbBr₃比率型荧光探针,该方法可通过荧光颜色变化(绿→黄→红)直接指示

THM 浓度,且该方法对 THM 的肉眼检测具备高灵敏度、高选择性和优异的抗干扰能力。

1.3 电化学分析

电化学分析通过电化学反应产生的电流或电位变化对物质的含量或性质进行检测和分析。这类传感器具有操作简单、响应快速、成本低廉、选择性强等特点^[46-47],已广泛应用于水、土壤、食品及其他环境介质中农药残留的检测^[1,48]。除传统电化学酶传感器和电化学免疫传感器外,研究者还开发了分子印迹电化学传感器、MOTs 电化学传感器和纳米材料电化学传感器等新型传感器。

1.3.1 分子印迹电化学传感器

分子印迹电化学传感器以分子印迹聚合物(MIPs)为识别元素,通过特定的识别策略与目标分子特异性结合,进而实现高选择性检测,已广泛

应用于药物分子、环境污染物、生物分子的分析检测^[49]。MIPs 作为人工仿生识别受体,具有良好的机械稳定性和重现性,是电化学传感器中极具应用价值的功能材料。

镧系元素配合物具有发射带窄、斯托克斯位移大、激发态寿命长等特点,基于镧系金属离子和有机配体构建的金属有机凝胶(metal-organic gel, MOG)已成为电化学发光(ECL)领域的理想材料。Cai 等^[50]制备了镧系金属有机凝胶衍生材料(Tb-Ru-MOG/CeO₂),并将其作为纳米共反应加速器构建了一种超灵敏的 IMI 检测传感器,检测限低至 1.37 nmol/L。MIT 与电化学传感器的结合,不仅能够实现目标物的高灵敏度、高选择性检测,还可有效缩短检测时间。分子印迹电化学传感器的作用机制见图 7。

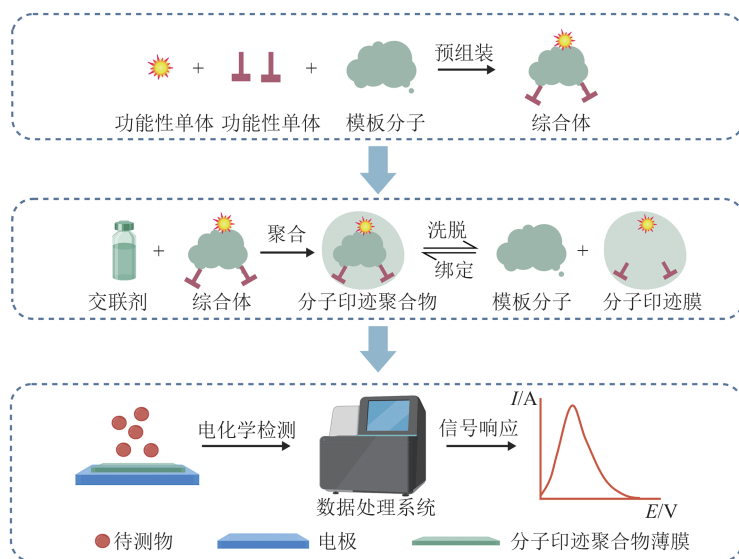


图 7 分子印迹电化学传感器作用机制

Fig. 7 Detection mechanism of electrochemical sensor based on molecular imprinting

此外,比率荧光传感器能够显著降低检测限、扩大线性检测范围,同时提升检测的稳定性和灵敏性。Wei 等^[51]构建了比率荧光分子印迹传感器,成功实现了 IMI 的特异性识别与定量检测,线性检测范围为 5~500 ng/mL,检测限低至 3.55 ng/mL。Dai 等^[52]将 MIT 与蓝光、红光碳点结合,构建了比率荧光传感系统,用于 CLO 的可视化、高选择性检测。由于 MIPs 在 GN 表面可形成单层均匀结构,其稳定性和特异性识别能力显著提升,因此 GN 常被用于传感器电极的修饰。Zhang 等^[53]提出了一种基于 GN 的分子印迹聚合物电化学传感器,用于 IMI 的

测定,线性检测范围为 0.5~15.0 $\mu\text{mol/L}$,检测限为 0.10 $\mu\text{mol/L}$ 。Kong 等^[54]构建了邻苯二胺分子印迹传感器,不仅提高了检测的灵敏度与选择性,还具备良好的稳定性和重复性。

1.3.2 MOFs 电化学传感器

MOFs 是由金属离子与有机配体通过配位键自组装形成的一类新型多功能结晶多孔材料。MOFs 的合成、构型和应用见图 8。MOFs 可作为电极材料或模板,经合成修饰或其他功能材料复合,可构建出具备优异电化学性能的传感器^[55]。

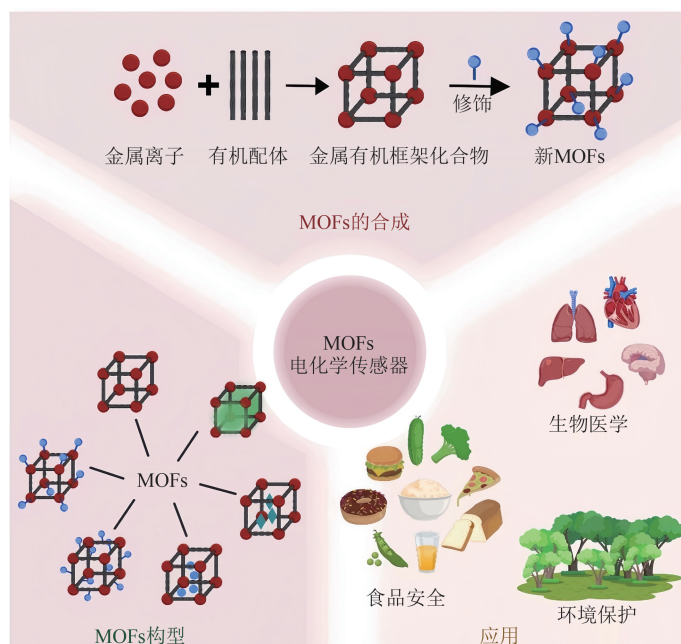


图8 MOFs电化学传感器的制备、构型和应用

Fig. 8 Design, configurations, and application of electrochemical sensors based on MOFs

由于MOFs具有高比表面积、可调节孔径及易于修饰的特性,在催化、气体吸附等领域展现出独特优势。其中MIL-101、ZIF-8和UIO等系列在水中能保持较高的稳定性。MIL-101系列凭借其优异的水稳定性、酸稳定性、高比表面积和高孔隙率等优势^[56],在电化学传感器构建中展现出显著优势^[57]。Ma等^[58]建立了分散固相萃取-液相色谱-质谱联用法,用于水环境样品中多种农药残留的检测,检测限低至0.02~0.10 ng/mL,加标回收率为81.3%~95.1%。Wang等^[56]通过热解铜基MOF与聚乙烯吡咯烷酮(PVP),成功制备出兼具良好亲水性和导电性的新型三维氮掺杂多级孔碳复合材料(3D N/Cu-HPC),并将其成功应用于燕麦、玉米和水稻中IMI、THM和DIN的测定,回收率为92.0%~100.9%。

此外,MOFs也被广泛应用于NEOs的固相萃取和富集。Huang等^[59]将多壁碳纳米管与NH₂-MIL-101(Fe)复合,并成功应用于食品基质中THM、IMI、CLO、IMZ、ACE、THD等多种农药残留的检测。Ghiasi等^[60]将GO和磁性介孔二氧化硅纳米颗粒整合至NH₂-MIL-101(Cr)中,合成了一种新型纳米复合吸附剂,可用于水果和水样品中IMI和ACE的超声辅助磁性固相萃取。Cao等^[61]采用恒温法合成UiO-66材料,并将其应用于

水样中THM、CLO、IMI、ACE和THD的分散固相萃取,该方法具有操作简便、灵敏度高、回收率高等优势。通过持续优化MOFs的结构和功能,可进一步提升传感器的性能。

1.3.3 纳米材料电化学传感器

纳米材料具备高电催化活性和大比表面积,可显著提高电子传递效率并赋予电极特定的理化性质^[62]。这类电化学传感器主要通过调控修饰电极的纳米材料组分,实现对农药残留的高灵敏度和高选择性检测。

其中,金属纳米颗粒和碳基纳米材料凭借其独特的物理、化学及电催化性能,在电化学传感器中展现出优异的应用潜力。Rashed等^[62]合成了一种新型三元纳米复合材料(AgNPs/介孔碳/赤铁矿),其中介孔碳凭借其高比表面积、高孔隙率、高导电性和高稳定性,有效提升了传感器对IMI的检测性能。由于GO具有优异的催化性能和电子传输效率^[63],是构建这类传感器的理想材料。Luo等^[63]构建了一种基于GO、AuNPs和 β -CD复合功能纳米材料的电化学传感器,用于IMI的检测,检测限为 1.33×10^{-10} mol/L。Urbanová等^[64]采用GO修饰的玻璃碳电极(GCE)制备了用于检测THM和IMI的传感器,该传感器的线性检测范围为10~200 μ mol/L,检测限分别为8.3、7.9 μ mol/L。Zhang等^[65]制备了一种基于 β -CD-GN修饰的

GCE,用于 PAI 的电化学分析,该体系展现出良好的电催化性能,检测限低至 0.11 μmol/L。

2 NEOs残留快速检测技术比较

为了更直观地比较和分析不同快速检测技术在农药残留检测中的应用,作者系统梳理了 9 种 NEOs 残留的快速检测方法,这些方法已被证实有效且在全球范围内广泛应用,见表 1。

免疫分析操作简便、耗时短且设备成本较低,

适用于现场快速检测及大规模筛查。然而,该技术易受有机溶剂和样品基质的干扰,且交叉反应风险较高。以 ELISA 为例,其检测限较低,但在复杂基质样本中易出现假阳性结果。而 SERS 通过内标归一化法,可将干扰误差控制在 5% 以内。这种差异反映出抗原抗体反应机制与标记物选择间的根本矛盾——灵敏度的提升往往伴随着操作复杂度的增加。与电化学分析相比,免疫分析的交叉反应率高达 15%~30%,而分子印迹电化学传感

表 1 农产品中 NEOs 残留快速检测技术及其应用						
Table 1 Rapid detection technologies and their application in the detection of NEOs residues in agricultural products						
NEOs	方法	线性检测范围	检测限	回收率	样品	参考文献
DIN	ELISA	1.0~30.0 ng/mL	0.6 ng/mL	92.5%~113.2%	水稻	[20]
	纳米材料电化学传感器	0.2~50.0 μmol/L	0.05 μmol/L	96.67%~103.65%	水稻	[66]
	分子印迹电化学传感器	1×10 ⁻⁷ ~1×10 ⁻² mol/L	0.35 μg/L	87.93%~106.43%	黄瓜	[67]
	MOFs 电化学传感器	1~60 μmol/L	0.01 μmol/L	92.0%~100.9%	燕麦、玉米和水稻	[56]
	纳米材料电化学传感器	0.5~60.0 μmol/L	0.001 μmol/L	92.1%~103.4%	苹果、西红柿和马铃薯	[68]
THD	ELISA	—	0.7 μg/L	80.3%~116.3%	农产品和土壤	[69]
	FIA	0.01~10.00 ng/mL	0.003 ng/mL	79.4%~118.6%	梨、橙子和黄瓜	[23]
	ELISA	10.30~2 110.00 μg/L	4.25 μg/L	85.27%~113.07%	番茄、梨和白菜	[21]
	FIA	—	0.5 ng/mL	81.7%~118.1%	糙米、番茄和梨	[24]
	SERS	1.0×10 ⁻⁴ ~1.0×10 ³ μg/mL	4.55×10 ⁻⁵ μg/mL	97.83%~114.23%	绿茶	[70]
IMI	ICA	0.04~3.00 ng/mL	0.04 ng/mL	80%~124%	番茄、玉米、胡萝卜和小米	[3]
	FRET	5×10 ⁻⁹ ~4 000×10 ⁻⁹ mol/L	8.23×10 ⁻¹⁰ mol/L	93.0%~105.6%	香蕉、苹果、卷心菜和黄瓜	[44]
	纳米材料电化学传感器	5×10 ⁻¹⁰ ~3 000×10 ⁻¹⁰ mol/L	1.33×10 ⁻¹⁰ mol/L	92.0%~110.0%	香蕉、芒果和白菜	[63]
	分子印迹电化学传感器	0.5~15.0 μmol/L	0.10 μmol/L	75%~78%	水稻	[53]
	纳米材料电化学传感器	0.1~20.0 μmol/L	0.011 μmol/L	97%~104%	卷心菜和黄瓜	[71]
THM	MOFs 电化学传感器	0.5~60.0 μmol/L	0.026 μmol/L	92.0%~100.9%	燕麦、玉米和水稻	[56]
	纳米材料电化学传感器	0.5~60.0 μmol/L	0.017 μmol/L	92.1%~103.4%	苹果、西红柿和马铃薯	[68]
	FIA	—	16 ng/L	77%~125%	马铃薯、黄瓜和苹果	[72]
	纳米材料电化学传感器	5×10 ⁻¹¹ ~5 000×10 ⁻¹¹ mol/L	9.81×10 ⁻¹² mol/L	90.5%~109.3%	香蕉、豇豆和卷心菜	[73]
	纳米材料电化学传感器	4.0×10 ⁻⁶ ~1.0×10 ⁻³ mol/L	9.32×10 ⁻⁷ mol/L	—	玉米和豆类	[74]
ACE	MOFs 电化学传感器	0.5~60.0 μmol/L	0.062 μmol/L	92.0%~100.9%	燕麦、玉米和水稻	[56]
	纳米材料电化学传感器	1~60 μmol/L	0.007 μmol/L	92.1%~103.4%	苹果、西红柿和马铃薯	[68]
	SERS	1~20 μg/g	23.7~36.4 ng/g	73.5%~112.8%	梨和桃	[39]
	SERS	25~250 nmol/L	6.8 nmol/L	86.1%~100.3%	苹果	[75]
	FRET	10~90 ng/mL	6.33 ng/mL	92%~110%	山药和苦参	[76]
CLO	SERS	1~20 μg/g	33.7~68.8 ng/g	73.5%~112.8%	梨和桃	[39]
	FIA	0.021~973.000 μg/L	0.021 3 μg/L	79.3%~108.7%	小麦、玉米、番茄、黄瓜、菠菜、卷心菜、水稻、苹果、梨和葡萄	[22]
	FRET	20~600 μg/L	5.527 μg/L	81.99%~106.64%	卷心菜、番茄和梨	[77]
	纳米材料电化学传感器	1.0×10 ⁻⁷ ~5.0×10 ⁻⁵ mol/L	4.0×10 ⁻⁸ mol/L	90.0%~99.4%	苹果	[78]
	FIA	0.018~2 713.680 μg/L	0.018 μg/L	81.3%~117.7%	土壤、梨、番茄、水稻、苹果、卷心菜和黄瓜	[79]
IMZ	ELISA	0.55~3.82 ng/mL	0.55 ng/mL	72.3%~101.3%	卷心菜、大米、苹果、白菜、梨和番茄	[80]
	ELISA	5.19~2 762.00 μg/L	2.12 μg/L	85.27%~113.07%	番茄、梨和白菜	[21]

器通过引入 MIPs,显著降低了交叉反应率,证明该技术可提升对农药的特异性识别能力,有效解决了交叉反应难题。

光学分析操作便捷,适合批量样品的快速筛选与无损检测,但该技术对设备装置要求极高,通常需根据具体应用场景构建适配样品的数据库及模型,且在高通量检测中易受荧光信号稳定性及背景干扰的限制。拉曼光谱与荧光光谱因其技术原理不同,应用场景差异明显。拉曼光谱依赖特征峰识别,在苹果汁等透明基质中可实现目标物的快速定量^[75],但在浑浊样品中信号衰减达 60%;荧光光谱虽可通过时间分辨技术抑制背景干扰,但其设备成本较传统方法增加了 5~8 倍。因此,光学分析需平衡光谱选择性和经济性之间的矛盾。研究表明,SERS 对 CLO 的增强因子差异达 3 个数量级,这可能与基底纳米结构的热力学稳定性差异有关,未来应聚焦标准化 SERS 基底制备工艺的优化。

相较于前 2 种方法,电化学分析测定成本最低、操作相对简单,且具备超高灵敏度和强适用能力。如分子印迹电化学传感器能够有效解决传统样品前处理复杂和分析检测中的非特异性吸附问题,显著提高了检测的准确性^[81]。但该技术仍需特定的前处理步骤,样品基质的复杂性可能影响检测结果的准确性^[1]。与免疫分析相比,电化学分析抗基质干扰能力更强,但其重复使用次数远低于免疫试纸条,这表明纳米材料界面稳定性是电化学器件的主要短板。研究显示,将分子印迹膜与丝网印刷电极结合,既可保留电化学检测的实时性,又能提升抗干扰能力。然而,在多功能集成方向上仍存在技术联用的适配矛盾。

为更系统地评估 NEOs 残留传统检测方法与新型快速检测技术的适用性,作者从检测限、灵敏度、操作复杂度等核心指标对两者进行了对比分析,见表 2。

表 2 NEOs 残留传统检测方法与新型快速检测技术对比
Table 2 Comparison between conventional and novel rapid detection technologies

检测方法	检测限/ (ng/mL)	灵敏度	特异性	操作 复杂性	成本	检测 时间	适用场景	优点	缺点
传统检测方法	0.01~1.00	高,适用于痕量分析	强,依赖色谱分离与质谱鉴定	较高	高	长	实验室确证分析、法规合规性检测	高准确性、高灵敏度、适合复杂样品分析	设备昂贵且笨重、前处理较复杂、无法满足现场需求
新型快速检测技术	0.001~10.000	强,但易受基质干扰	高,但交叉反应率可能较高	较低	低	短	现场快速筛查	快速便捷、操作简单、适合大规模筛查	基质效应显著、部分技术稳定性不足、存在交叉反应

综上所述,当前 NEOs 残留检测技术存在两大问题。一是性能指标与实际应用场景脱节,部分研究过度追求低检测限,与田间快速筛查等实际需求相悖;二是技术评价标准不统一,不同研究采用的验证参数存在差异,如免疫分析侧重回收率,电化学分析侧重电极稳定性与重现性,导致不同技术间缺乏统一的比较基准。针对上述问题,后续研究者应建立基于不同农产品基质特性与应用场景的多元化评价体系,明确检测限、检测通量及检测成本的权重分配。在 NEOs 残留检测中,应系统评估检测限、定量限、线性检测范围、精密度及准确度等核心指标,结合农产品基质特性筛选最优检测方案。

3 展望

随着 NEOs 在农业生产中的广泛应用,其残留问题对生态环境、人类健康的威胁已引起广泛关

注。为应对 NEOs 残留引发的环境污染和食品安全问题,目前已经建立了多种适用于 NEOs 残留的快速痕量检测方法。NEOs 残留快速检测技术虽然在灵敏度、检测时间、抗基质干扰能力等方面的优势显著,但存在成本高、样品前处理复杂、基质效应干扰和假阳性等问题,仍是该领域亟待攻克的关键瓶颈。因此,未来 NEOs 残留快速检测技术的研究应聚焦以下几个方向。第一,突破样品前处理技术瓶颈。针对液液萃取等传统方法耗时长、易污染等问题,应开发更高效、简便的样品前处理技术,以提高检测效率和准确性。第二,提高检测灵敏度与选择性。传统仪器检测方法虽然精度较高,但实际应用中受多种因素限制,光学分析和电化学分析有望成为未来重点发展的方向。第三,开发微型化现场检测装置。面向农产品中 NEOs 残留的检测需求,研发适配田间场景的微型化装置,重点依托生物传感器技术实现多残留快

速同步检测,并结合智能化、自动化技术进一步提高检测效率和准确性。未来,NEOs 残留检测技术将持续优化和完善,有望突破传统检测技术瓶颈,最终实现 NEOs 残留的高效检测和有效管控。

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