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环境中典型植物生长调节剂分析测试技术研究进展

胡晓蕾[1,2], 陈亮[1,2*], 侯杰[1,2], 吴少培[3], 王蕾[3]
(1. 天津大学水利工程仿真与安全国家重点实验室, 天津 300350;
2. 天津大学建筑工程学院, 天津 300350;
3. 启衡(天津)检测科技有限公司, 天津 300350)

摘要: 近年来,植物生长调节剂被广泛应用于农业领域,主要有加速或延缓种子萌发、打破植物休眠、刺激或减少芽伸长、诱导开花结果以及影响衰老过程等功效,对植物的生长有着重要作用。但是,由于其施用量不断增加,导致植物生长调节剂在环境介质中被多次检出,且经过一系列环境行为产生的中间产物可能具有更强的毒性,严重威胁环境安全乃至人体健康。通过总结植物生长调节剂分析测试相关国内外研究文献发现,果蔬、肥料和土壤等固态基质样品的前处理多采用固相萃取方法,而水体、食用油和营养液等液态基质样品的前处理则多以液液萃取方法为主。同时,大多数植物生长调节剂的辛醇水分配系数在 0~4 之间,具有极强的亲水性,而高效液相色谱-串联质谱法(HPLC-MS/MS)具有较低检出限和较高准确度等优点,使其成为目前使用最多的植物生长调节剂分析测试技术。其次,部分植物生长调节剂沸点低、易挥发,也可以采用气相色谱法或气相色谱-质谱联用法(GC-MS)进行检测。几种常用分析测试技术检出限的大小顺序大致为:气相色谱法>液相色谱法>色谱-质谱联用法,其中,色谱-质谱联用法的仪器检出限可低至 10^{-5}mg/kg。但是,由于大部分植物生长调节剂溶解度高、自然衰减速率快,导致其在土壤和水体等复杂环境基质中的检出浓度偏低,关于土壤和水体中痕量植物生长调节剂及其中间产物的分析测试问题仍亟待解决。未来,相关研究应聚焦于植物生长调节剂中间产物的分析测试,并开发基于新材料、新技术的植物生长调节剂分析测试方法。

关键词: 植物生长调节剂; 固相萃取; 液液萃取; 高效液相色谱法; 色谱-质谱法; 检出限

要点:

(1) 固相萃取或液液萃取是植物生长调节剂最常用的前处理方法,QuEChERS 方法是最常用的净化技术。

(2) 高效液相色谱-串联质谱法(HPLC-MS/MS)是植物生长调节剂最常用的分析测试技术,适用于果蔬、肥料等不同环境介质中植物生长调节剂的检测。

(3) 考虑到植物生长调节剂自然衰减速率较快且其中间产物毒性较高,未来研究应重点关注痕量植物生长调节剂及其中间产物的分析测试。

中图分类号: S482.8; O657.7; O657.63　　**文献标识码:** A

植物生长调节剂被定义为天然存在或人工合成的化合物[1],在农业生产中主要有加速或延缓种子萌发、打破植物休眠、诱导开花结果以及影响衰老过程的功效[2-3],对植物的生长有着重要作用。据 2015 年统计数据显示,过去十年间植物生长调节剂在国际市场上的贸易额达到约 16 亿美元[4],在农业生产中被广泛使用。中国作为世界上使用植物生长调节剂较多的国家之一,2010—2016 年间平均使用量为 65×10^7kg/年[5]。截至 2021 年 5 月,中国共登记了 1175 个植物生长调节剂产品[6]。但是,植物生

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第一作者: 胡晓蕾,硕士研究生,主要研究方向为水资源、水环境保护与修复。E-mail: huxiaolei@tju.edu.cn。
通信作者: 陈亮,博士,副教授,主要研究方向为渗流过程水量水质变化及污染物治理新技术。E-mail: liangchen@tju.edu.cn。

长调节剂使用过程中存在的大量滥用、误用现象不仅减少了农作物的产量,而且加剧了其在环境中的残留,特别是在果蔬等农产品中的残留尤为显著。颜伟华等[7]在 259 份豆芽样品的 146 份中检出多效唑、赤霉素和噻苯隆等植物生长调节剂,芒果中 6-苄氨基嘌呤的含量高达 0.50mg/kg[8]。同时,在水体和土壤中也检出多种植物生长调节剂。黄思静等[9]检测了水源水、出厂水和末梢水 8 份水样中 7 种目标青霉素的残留,测定值在 4.56~20.79ng/L 之间。汤涛等[10]对浙江和山东两省的棉花田土壤样品中乙烯利进行检测,检出范围分别为 0.17~8.90mg/kg 和 0.19~4.00mg/kg。另外,绝大部分植物生长调节剂都有毒性,且部分进入土壤后会发生吸附、解吸、水解、光解和微生物降解等环境行为并产生分解产物[11],而分解产物多具有更高的毒性。例如,赤霉酸的水解产物异构赤霉酸会造成小鼠肾脏和肝组织细胞坏死,水解副产物赤霉烯酸和羟基赤霉酸等毒性也均比赤霉酸强[12-13]。

为评估植物生长调节剂残留是否会对环境及人体健康造成威胁,一些高效、快速的分析测试技术被用来对植物生长调节剂进行定性和定量分析,以判断其残留是否满足相关标准。目前,分析测试技术主要包括气相色谱(GC)和气相色谱-质谱联用法(GC-MS)[14-16]、高效/超高效液相色谱(HPLC/UPLC)和高效/超高效液相色谱-串联质谱法(HPLC/UPLC-MS/MS)[17]、离子色谱法(IC)[18]、分光光度法(SP)[19]、毛细管电泳分析法(CE)[20]、酶联免疫法(ELISA)[21]和电化学传感器法[22]等。其中,由于植物生长调节剂双键、羧基等结构特性及其较高水溶性,色谱[23]以及色谱-质谱联用[24]成为目前比较成熟且被广泛应用的分析测试技术,在相关植物生长调节剂分析测试的研究文献中占比高达 70%(分别为 32.84%和 36.82%)。早在 2000 年,Hau 等[25]采用液相色谱-电喷雾电离串联质谱法测定了食品中的矮壮素,最高检出浓度达到 5.50mg/kg。Liu 等[26]将荧光技术与 HPLC-MS 联用,并结合微波辅助萃取-衍生化的方法,对食用油中的赤霉酸、吲哚乙酸、吲哚丙酸、吲哚丁酸、1-萘乙酸和 2-萘乙酸等 6 种酸性植物生长调节剂进行了检测,结果显示非转基因菜籽油中植物生长调节剂检出浓度最高,在 2.93~10.85mg/kg 之间。2022 年,陈建波等[27]将高效液相色谱与附蒸发光散射检测器联用,检测了水溶性肥料中季铵盐类植物生长调节剂,13min 内实现了目标物的完全分离,在 10%的样品中检测出植物生长调节剂的残留。

本文总结了果蔬、肥料和土壤等固态基质和水体、食用油和营养液等液态基质中典型植物生长调节剂常用的固相萃取、液液萃取等前处理方法以及高效液相色谱-质谱联用法和超高效液相色谱法等分析测试技术。同时,考虑到植物生长调节剂较强的自然衰减能力及其中间产物的高毒性,并结合植物生长调节剂的特殊结构及性质系统归纳了不同测试技术的优缺点及适用范围,以全面了解植物生长调节剂前处理和分析测试现状,为后续研究植物生长调节剂的分析测试、迁移转化和污染评估与治理提供文献支撑。

1　植物生长调节剂的特点

1.1　植物生长调节剂的分类及作用

根据植物生长调节剂的性质和功效,可以将其分为三大类:植物生长促进剂、植物生长抑制剂和植物生长延缓剂[5](表 1)。植物生长调节剂的作用多种多样。例如,Chen 等[28]发现施加赤霉素可以增加器官伸长率,进而增加番茄的形状指数。Guzmán 等[29]对生长素、吲哚丁酸和赤霉素的组合能否改善“优质无籽”品种葡萄的品质属性进行了研究,结果表明使用该组合后,果实的硬度和冷藏 60 天后的新鲜度都得到了提高。李响等[30]用外源乙烯、脱落酸及乙醇对薄皮甜瓜的研究表明,脱落酸和乙烯能够促进果实的软化。Lal 等[31]通过喷施不同浓度多效唑,最高可使梨的产量增加 34%。其中,赤霉素、乙烯利以及多效唑和希效唑是目前使用和研究比较广泛的植物生长调节剂[7,10]。

表 1　植物生长调节剂的分类及作用[5]

Table 1　Classification and function of plant growth regulators[5]

植物生长调节剂分类	作用	典型产品
植物生长促进剂	促进机体细胞分裂和新生器官分化	生长素、细胞分裂素、赤霉素、胺鲜酯、乙烯利及油菜素甾醇类化合物等
植物生长抑制剂	导致茎伸长,从而抑制植物的顶端优势,促进植物侧叶增多	肉桂酸、香豆素和脱落酸等
植物生长延缓剂	抑制植株节间伸长,使得植株变矮	矮壮素、多效唑、烯效唑、氟节胺和吡啶醇等

1.2　典型植物生长调节剂的化学结构式和理化性质

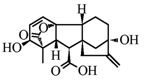
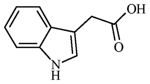
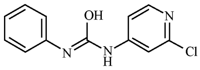
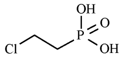
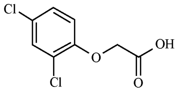
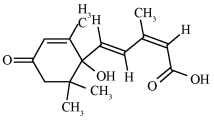
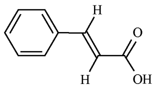
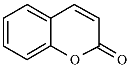
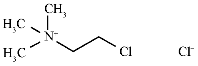
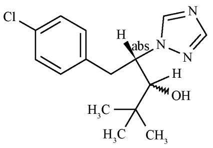
典型植物生长调节剂的化学结构式和理化性质如表 2 所示。大部分植物生长调节剂水溶性较高，20℃左右时水中溶解度在 0.02~8g/L 之间；同等温度下，乙烯利水中溶解度高达 1000g/L，远高于其他植物生长调节剂。而且，大部分植物生长调节剂正辛醇水分配系数在 0~4 之间，表明其具有较强的极性和亲水性。另外，植物生长调节剂的官能团种类也较丰富，大部分含有双键，吲哚乙酸、脱落酸和肉桂酸等酸性植物生长调节剂含有羧基，芳环存在于氯吡脲、肉桂酸等植物生长调节剂中，其他植物生长调节剂还含有羟基、醚键和氨基等官能团。

1.3　植物生长调节剂的毒性

植物生长调节剂属于微毒或低毒农药，多直接作用于植物，并可能残留于果蔬或进入土壤和地下水系统，进而威胁环境安全和人体健康。例如，多效唑可以增加肝细胞的氧化应激和凋亡率[32]，造成斑马鱼胚胎发育不良[33]，若残留于土壤中还会减缓马铃薯生长速率[34]；小鼠孕早期暴露于乙烯利中会降低血清孕激素水平[35]，并损害体细胞组织[36]；另外，暴露于 2,4-二氯苯氧乙酸中，会损害斑马鱼幼虫视网膜结构[37]，影响其肝细胞代谢[38]，并增加肺癌患病率风险[39]。

表 2　部分典型植物生长调节剂的化学式、结构式和常用理化性质

Table 2　Chemical formula, structural formula and common physical and chemical properties of the typical plant growth regulators

植物生长调节剂分类	典型代表	化学式	熔点（℃）	沸点（℃）	密度（g/cm^3）	水中溶解度（g/L）	正辛醇-水分配系数	结构式
植物生长促进剂	赤霉酸	$C_{19}H_{22}O_6$	227	628.60±55	1.50±0.10	20℃：5.00	0.01	
	吲哚乙酸	$C_{10}H_9NO_2$	165~169	415	1.36	20℃：8.00	1.43	
	氯吡脲	$C_{12}H_{10}ClN_3O$	170	308.40	1.42	22℃：0.04	3.83	
	乙烯利	$C_2H_6ClO_3P$	70~72	333.40	1.57	23℃：1000	-1.42	
	2,4-二氯苯氧乙酸	$C_8H_6Cl_2O_3$	140.5	160	1.56	20℃：0.89	2.59	
植物生长抑制剂	脱落酸	$C_{15}H_{20}O_4$	163	458.70	1.19	20℃：3~5	1.70	
	肉桂酸	$C_9H_8O_2$	133	300	1.25	20℃：0.40	2.41	
	香豆素	$C_9H_6O_2$	68~73	298	0.94	25℃：2.50 100℃：20	1.39	
植物生长延缓剂	矮壮素	$C_5H_{13}Cl_2N$	239~243	260.30	1.22	20℃：0.74	0.93	
	多效唑	$C_{15}H_{20}ClN_3O$	165~166	460.90	1.19	20℃：0.03	2.99	

2　不同环境介质中植物生长调节剂分析检测前处理方法

由于样品中多含有大量杂质干扰检测,因此合适的前处理方法可提高测试结果的准确性。但是,样品前处理过程所占工作量超过整个分析测试工作的 70%,且最终检测结果中约 50%的误差来源于前处理[40]。所以,建立快速、简便和稳定的前处理方法,可有效地提高分析检测效率及准确度。目前,检出植物生长调节剂的环境介质形态主要分为两种(表 3):固态基质样品(果蔬、肥料和土壤等)和液态基质样品(水体、油和营养液等),相关涉及的前处理方法也多针对这两种不同形态的环境基质。

2.1　固态基质样品

涉及植物生长调节剂的固态基质主要包括果蔬、肥料和土壤等。其中,果蔬是植物生长调节剂检出最频繁的固体基质,而肥料和土壤等基质中也已检出部分植物生长调节剂。固态基质样品的前处理过程可分为提取和净化两大部分。其中,QuEChERS 方法是应用最广泛的固体基质样品前处理方法。

(1)提取

索氏提取是一种经典的液固提取技术,可被用于固态基质中植物生长调节剂的提取,并可以配合超声仪进行提取[46]。超声提取通过高频率超声波增加固体样品中待测物的溶出速率,能够大大缩短提取时间[47]。此外,加速溶剂萃取通过增大有机溶剂的沸点,也可以提高待测样品中植物生长调节剂在较高温压下的提取效率[48-49];超临界流体萃取则以超临界流体代替有机溶剂,对待测样品中植物生长调节剂进行提取[50-51];微波辅助萃取利用微波,使待测样品中植物生长调节剂的解吸速率及其在两相中的分配速率加快,减少了试剂消耗量,同时提高了提取效率[52]。

(2)净化

固相萃取技术具有溶剂耗量少、对实验条件要求较低的优点[53-54]。目前,以固相萃取为基础,逐渐发展形成了许多新型固相萃取方法,主要包括固相微萃取、磁性固相萃取、分散固相萃取和全自动固

表 3　植物生长调节剂分析测试时固态基质样品和液态基质样品常用的前处理方法

Table 3　Common pretreatment methods of solid matrix samples and liquid matrix samples for the analysis and test of the plant growth regulators

介质类型		测定物质	样品前处理方法	提取剂	回收率(%)	参考文献
固态基质	肥料	茉莉酸、多效唑、水杨酸、反式玉米素、赤霉素、吲哚乙酸、脱落酸、芸苔素内酯、胺鲜酯	液液萃取	甲醇	92.00~104.70	[41]
	果蔬	赤霉酸、脱落酸、吲哚丙酸、对氯苯氧乙酸、噻苯隆、4-苯氧基乙酸、调果酸、2,4-二氯苯氧乙酸、氯吡脲、抗倒胺、环丙酸酰胺、吲哚乙酸、6-氨基嘌呤、吲哚丁酸、抗倒酯、多效唑、烯效唑、抑芽唑	QuEChERS	乙酸-乙腈溶液	70.10~116.20	[42]
	大米	五氟磺草胺、哌草丹、乙草胺、多效唑、烯效唑、矮壮素、脱落酸、2,4-二氯苯氧乙酸	QuEChERS	乙腈-水-甲酸溶液	75.10~115.00	[43]
	黄瓜番茄	4-氯苯氧乙酸、6-糠基氨基嘌呤、吲哚丁酸、α-萘乙酸、氯吡脲等	分散固相萃取	乙腈-二氯甲烷(含 0.5%甲酸)	71.90~113.80	[44]
	豆芽	4-氯苯氧乙酸、2-萘乙酸、吲哚乙酸、吲哚丁酸、4-氟苯氧乙酸、2,3,5-三碘苯甲酸、4-溴苯氧乙酸、2,4-二氯苯氧乙酸、2,4,5-三氯苯氧乙酸、2,6-二甲基苯氧乙酸	超声-固相萃取	乙腈	96.30~102.10	[20]
液态基质	植物营养剂	赤霉酸、多效唑、异戊烯腺嘌呤、5-硝基邻甲氧苯酚钠、6-苄基腺嘌呤、4-氯苯氧乙酸、吲哚丁酸、烯效唑、4-氟苯氧乙酸、氯吡脲、噻苯隆	超声-固相萃取	甲醇	92.50~103.50	[45]
	食用油	赤霉酸、吲哚乙酸、吲哚丙酸、吲哚丁酸、1-萘乙酸、2-萘乙酸	微波辅助萃取	甲醇	96.10~104.40	[26]

相萃取等[55]。随着研究深入,学者们已经研究出许多新型材料构建的吸附剂,例如新型磁性共价有机骨架材料[56]、氨基修饰的 Scholl 耦合介孔聚合物[57]、新型磁性β-环糊精修饰氧化石墨烯[58]和磁性碳化硼纳米片[59]等,都可用于萃取固态基质样品中的植物生长调节剂。

此外,QuEChERS 方法因其快速、便宜、有效、可靠和安全的特点,成为固态基质样品中植物生长调节剂检测使用最广泛的前处理方法[60]。该方法通过乙腈或者酸化乙腈提取植物生长调节剂,并进行盐析分层,再通过分散固相萃取,利用合适的吸附剂将植物生长调节剂与乙腈中大部分干扰物结合,从而达到净化的目的[61]。但当基质较复杂时,该方法存在富集倍数不高、净化效果不够理想等问题。毕军等[62]通过冷冻诱导液液萃取技术,选择 40%乙腈水溶液处理样品,改良优化了 QuEChERS 技术,使样品的相对回收率均可达到 70%~120%。

2.2 液态基质样品

水体、食用油和营养液是植物生长调节剂被检出最频繁的液态基质。目前,液液萃取是液态基质最常用的萃取方法。对于萃取剂的选择,赤霉酸和乙烯利等植物生长调节剂的正辛醇水分配系数小于 1,为强极性化合物,可用甲醇、乙醇和丙酮等亲水性有机溶剂萃取;氯吡脲和多效唑等其余大部分植物生长调节剂的极性相对较弱,但与苯和氯乙烷等其他类别的化合物(正辛醇-水分配系数>10)相比,仍属于极性较强的范畴,因此,萃取剂不仅可以用甲醇,还可用乙酸乙酯和氯仿等不溶于水的极性有机溶剂。虽然液液萃取对萃取剂的要求较多,但是绝大部分植物生长调节剂高水溶性的特性,使其常通过 HPLC 或 HPLC-MS/MS 直接检测,省去了复杂的提取和净化等前处理步骤。此外,由于一些植物生长调节剂色谱特性差或不易被检测,还需要进行衍生化处理[26],从而将待测组分转化成适合被分析的衍生物。

3 植物生长调节剂分析测试技术

大部分植物生长调节剂存在羟基、羧基和芳环等官能团,且辛醇水分配系数小于 4、亲水性较强,因此具有前处理简单、快速便捷等优点的 HPLC/UPLC-MS/MS 成为应用最广泛的分析测试技术。同时,植物生长调节剂进入土壤和水体等环境中,会发生吸附、解吸和微生物降解等环境行为并产生浓度较低的中间产物,若对中间产物进行定性、定量分析,则对仪器的检出限要求较高,这也是 HPLC/UPLC-MS/MS 被应用最多的原因之一。另外,部分植物生长调节剂由于其沸点较低、易挥发,需采用 GC 或 GC-MS 进行分析测试,但在使用 GC 检测时大部分植物生长调节剂色谱特性差或不易被检测[63],需要提前进行衍生化处理。从普适性强弱的角度,植物生长调节剂相关测试技术主要包括 HPLC/UPLC-MS/MS[17,59]、HPLC/UPLC[64]、GC-MS[65-66]、GC[63]、IC[67]、SP[19]、ELISA[68]、CE[20]、电化学传感器[22]及微孔侧流免疫层析法[69]等。

3.1 高效液相色谱法、超高效液相色谱法及液相色谱-质谱联用法

高效液相色谱法(HPLC)具有操作简单、准确度高、分析周期较短、前处理较为方便等优点,可用于多种植物生长调节剂的同时检测[70]。但是,当样品基质比较复杂时,这种技术的选择性和灵敏度不高,且维修费用相对较高。与 GC 相同,为提高检测效率与准确度,HPLC 也常与质谱联用,具有样品前处理简便、特异性更强、灵敏度更高和定性能力更好等特点[71-72]。

目前,大部分植物生长调节剂水中的溶解度(20℃)在 0.50~10g/L,且自然分解转化速率较快,在土壤和地下水中的残留极少,对分析测试技术检出限要求较高。同时,绝大部分植物生长调节剂的辛醇-水分配系数在 0.50~4,亲水性强[73]。因此,HPLC/UPLC 和 HPLC/UPLC-MS/MS 几乎适用于所有植物生长调节剂的检出。但是,HPLC/UPLC 和 HPLC/UPLC-MS/MS 常被用于检测果蔬中植物生长调节剂的残留,其次是土壤和肥料,而自然水体中的相关研究较少。这可能是由于自然环境中植物生长调节剂自然衰减速率很快,导致其在地表水和地下水等自然水体中的残留极其微量甚至无法被直接检出。

通过 HPLC/UPLC 和 HPLC/UPLC-MS/MS 检测的不同环境介质中部分植物生长调节剂的检出限及植物生长调节剂回收率情况如表 4 所示。植物生长调节剂在使用 HPLC/UPLC 和 HPLC/UPLC-MS/MS 检测时,其平均回收率分别为 70.40%~110.00%和 69.10%~116.00%。其中,部分植物生长调节剂的回收率较低,例如水杨酸的回收率只有

表 4　高效液相色谱/超高效液相色谱及液相色谱-串联质谱法分析条件及部分植物生长调节剂检出情况

Table 4　Analysis conditions of high performance liquid chromatography/ultra-high performance liquid chromatography and liquid chromatography-tandem mass spectrometry and detection limits of some plant growth regulators

测试技术	固态/液态介质	PGRs 种类	色谱仪		检测器	检出限(土壤、肥料、果蔬 mg/kg;水 ng/L)	回收率(%)	参考文献
			型号	色谱柱				
HPLC	肥料	赤霉酸	Agilent 1260	Waters Atlantis T_3	UV	0.60	70.40~107.20	[74]
		脱落酸				0.20		
		萘乙酸				0.20		
		氯吡脲				1.90		
		烯效唑				5.10		
	土壤	多效唑	Waters Alliance 2695	Capcell PAK C18 MG Ⅱ		0.80×10^{-2}	98.30~102.10	[75]
	水体	氯吡脲	Shimadzu LC6A	Li-Chrosper 100 RP-8		0.40	90.00~92.00	[76]
UPLC	黄瓜	噻苯隆	Agilent 1290-infinity	Poroshell 120 EC-C18	DAD	1.90×10^{-2}	86.20~95. 00	[44]
	西瓜	氯吡脲				0.50×10^{-2}	85.00~90.50	
	番茄	脱落酸				1.90×10^{-2}	101.20~110.00	
	葡萄	2,4-二氯苯氧乙酸				7.60×10^{-2}	96.60~103.80	
HPLC-MS/MS	苹果	丁酰肼	Waters Alliance 2690	Hypersil APS-2	质谱	0.80×10^{-2}	98.0~102.0	[77]
	叶子					0.02	112.0~116.0	
	土壤	烯效唑	LC-20A	Agilent Poroshell 120 SB-C18		10^{-5}	84.00~87.00	[78]
UPLC-MS/MS	麦冬	多效唑	Waters Corp	Acquity HSS T_3 column	质谱	30	86.90~115.40	[79]
	土壤	烯效唑				50	81.30~108.20	
	水产品	水杨酸	Waters TQ-S	C18		0.26×10^{-2}	69.10~97.30	[80]
	肥料	嘧啶醇	Agilent 1290	Waters Acquity UPLC BEH C18		0.09~2.51	85.40~95.30	[81]
		调节膦						
		三唑醇						
		缩节胺						
	土壤	胺鲜酯	Agilent 1200	Varian VF-5ms	三重四极杆质谱	0.80×10^{-2}	89.40~103.30	[82]
UPLC-HRMS	水体	青霉素	Agilent 1290	ZORB-AX RRHD SB-C18	高分辨质谱	1~10	91.20~106.40	[9]

69.10%~97.30%[80],主要是其易水解特性导致。另外,相较于 GC 而言,HPLC 精密度和准确度也更高、检出限更低。例如,用 GC 和 HPLC 分别检测土壤中的多效唑,GC 检出限为 10mg/kg[23],而 HPLC 检出限可低至 0.80×10^{-2}mg/kg[74]。同时,HPLC 与质谱联用可使检出限进一步降低,用于检测土壤中烯效唑残留时,检出限可达 10^{-5}mg/kg[78]。

基于上述优点,植物生长调节剂进入土壤和水体等环境后通过水解、光解和微生物降解等环境行为产生的低浓度中间产物,也通常使用 HPLC/UPLC 或 HPLC/UPLC-MS/MS 技术进行检测。例如,Zhang 等[12]将 LC-MS 与离子阱(QIT)和飞行时间(TOF)技术结合,对赤霉酸的水解产物异构赤霉酸及水解副产物赤霉烯酸和羟基赤霉酸进行了检测。

3.2　气相色谱法和气相色谱-串联质谱法

气相色谱法(GC)具有低成本、易维护的优点,且气相色谱-串联质谱法(GC-MS)已成为一种常规测试技术[64]。但是,GC 和 GC-MS 受样品基质干扰影响较大,对前处理方法要求很高。另外,受不同植物生长调剂物理化学性质的影响(如沸点超过 400℃的脱落酸和吲哚乙酸等,或含羟基、羧基的氯吡脲及肉桂酸等),大部分植物生长调节剂的气相色谱特性差(表 2),且不易被检测。例如,李忠煜等[66]使用 GC-MS 检测土壤中酚类化合物时,需提前进行衍生化处理,使待测物质转化成适合被分析的衍生物。另外,衍生化反应还能够改善化合物的分离度和热稳定性,使其利于被检测。

GC 和 GC-MS 检测不同环境介质中的部分植物生长调节剂的检出限及回收率情况如表 5 所示。可

表 5　气相色谱法及气相色谱-质谱联用法分析条件及部分植物生长调节剂检出情况

Table 5　Analysis conditions of gas chromatography and gas chromatography-mass spectrometry and detection limits of some plant growth regulators

测试技术	固态/液态介质	PGRs 种类	色谱仪		检测器	检出限 (mg/kg)	回收率 (%)	参考文献
			型号	色谱柱				
GC	肥料	胺鲜酯 多效唑 烯效唑	Agilent 7890B	HP-5 毛细管柱	FID	10.0	80.60~97.10	[23]
	杨梅 苹果 枣树 卷心菜 西兰花	2,4-二氯苯氧乙酸 1-萘乙酸 吲哚乙酸 吲哚丁酸	Agilent 7890A	HP-5 毛细管柱		12.0 23.0 15.0 18.0	83.00~96.00	[83]
	水体	胺鲜酯	Varian CP-3800	CP 7625		/	79.00~107.00	[84]
	土壤	多效唑	Agilent 7890A	HP-5 毛细管柱	NPD	0.03	72.50~108.80	[85]
GC-MS	豆芽 番茄	对氯苯氧乙酸 2,4-二氯苯氧乙酸 1-萘乙酸 吲哚乙酸 吲哚丁酸	Agilent 7890A/5975C	HP-5MS	质谱	1.50×10^{-2}	70.00~127.00	[86]
	土壤	胺鲜酯	Agilent 6890-5975B	HP-5MS		0.10×10^{-2}	83.00~98.50	[87]
		多效唑	GCMS-QP2010	VF-1701 毛细管柱		0.42×10^{-2}	106.0~124.0	[88]

以看出，植物生长调节剂在使用 GC 和 GC-MS 检测时，其平均回收率分别为 72.50%～108.80% 和 70.00%～127.00%。为了进一步降低检出限，GC 常与质谱联用，以满足低浓度植物生长调节剂残留的检测。例如，土壤中较常检测出的多效唑和烯效唑等植物生长调节剂，使用 GC 检测时的检出限为 0.03mg/kg[85]，而 GC 与质谱联用后检出限降低至 0.42×10^{-2}mg/kg[88]。

3.3　离子色谱法

离子色谱法（IC）属于 LC 的分支[89]，可用于检测果蔬中植物生长调节剂。例如，Muhammad 等[90]利用 IC 结合荧光技术检测了 10 种食品中萘乙酸的含量，检出限范围为 0.08～6.60ng/kg；Melton 等[91]利用混合离子色谱-串联质谱法（IC-MS/MS）同时测定了果蔬中乙烯利和草甘膦，检出限为 0.05 mg/kg，平均回收率在 83.0%～112.0%。Bauer 等[92]用优化的 IC-MS/MS，测定了番茄、苹果和柠檬中的乙烯利，检出限为 0.01mg/kg，回收率均为 100.0%。该技术操作简便、经济，并且更多地以试剂盒的形式提供，可实现快速检测，但其灵敏度较低，主要用于果蔬等可能检出的高浓度植物生长调节剂介质。

3.4　分光光度法

分光光度法（SP）因其快速、准确、成本低及耗时短等优点，常用于现场快速测定。张莉等[93]采用快速 SP 技术同时检测了地下水中的赤霉素和草甘膦，检出限分别为 0.48μg/L 和 0.82μg/L，平均回收率分别为 69.40%～73.20% 和 90.30%～106.50%，并发现赤霉素在一定程度上会使草甘膦的回收率增加 10%左右。黄报亮等[94]和张璇等[95]检测了水溶液中除草剂氰尿酸及食品保鲜剂茶多酚和植酸的残留，平均回收率分别为 98.10%～102.00%、97.50%～102.50% 和 96.36%～102.24%。Maragou 等[96]通过 IC-间接 SP 技术检测了农药制剂中的乙烯利，改进后两种方法的平均回收率分别为 100.4% 和 99.6%，用第二种方法检测实验样品中乙烯利的含量范围在 481±5.90g/L。

3.5　其他技术

酶联免疫技术（ELISA）解决了 GC 存在的分析物易分解的技术难题。吴璟等[68]建立的直接竞争 ELISA 技术，实现对饼干、薯片及咖啡中丙烯酰胺的定量分析，平均加标回收率为 83.60%～112.70%，检出限为 3μg/L。Yi 等[97]开发了一种基于单克隆抗体的 ELISA 技术检测了植物中的茉莉酸甲酯，检

出限为 0.20μg/L。但是，ELISA 技术在同时分析多种类型残留组分时存在较大困难，用于分析结构相似的化合物时会发生不同程度的交叉反应等[98]。

毛细管电泳技术（CE）的分离效率高、耗时短，且有机试剂用量少[98]，不仅在医学、生物学、化学及农学等多方面应用极其广泛，也适用于分析测试大多数植物生长调节剂。张玉芬等[99]采用 CE 技术测定了番茄中 2，4-二氯苯氧乙酸的残留量，平均回收率在 98.20%～104.60%之间，检出限为 0.94mg/L。白新伟等[20]使用该技术对豆芽中 10 种植物生长调节剂残留进行检测，平均回收率为 96.30%～102.10%，检出限为 0.04～0.06μmol/L。陈宗保[100]采用聚合物整体柱微萃取-CE 技术测定了食品中萘乙酸等 5 种植物生长调节剂的残留，平均回收率范围为 87.30%～107.40%，检出限为 0.01～0.02mg/L。

电化学传感器法因其使用成本低、操作简单、检测时间短等优点[101]，逐渐被广泛研究和关注。该技术可以用于检测在电极表面发生有效电化学反应，且具有典型电化学结构特征的植物生长调节剂，例如水杨酸、茉莉酸甲酯、脱落酸和吲哚乙酸等。Wang 等[102]以类石墨氮化碳作为光活性材料，采用石墨烯量子点作为改进剂，并使用金纳米颗粒作为 DNA 探针的固定基质建立了光电化学传感法对玉米素进行捕获识别，回收率在 94%～105%。Zhu 等[103]通过结合具有高电催化活性的分子印迹聚合物和基于离子液体的石墨烯制备的新型复合材料提高了 6-苄基氨基嘌呤的检测效率，检出限可达 0.20μmol/L。Li 等[104]采用不锈钢丝作为电极，通过电沉积和电聚合作用依次形成石墨烯复合膜和番红花红聚合膜，增强了电极对吲哚乙酸的敏感程度，检出限低至 43pg/mL，实现了微电化学传感器检测植物体内吲哚乙酸的首次应用。

微孔侧流免疫层析法的前处理简单便捷、快速灵敏，但只能检测出结果呈阴性或呈阳性[69]，适合对样品进行快速筛选。华彦涛等[69]使用微孔侧流免疫层析法检测出农产品中存在 2，4-二氯苯氧乙酸（检出限为 0.05μg/mL），并能同时检测与 2，4-二氯苯氧乙酸结构类似的 4-氯苯氧乙酸和 2，4，5-三氯苯氧乙酸（检出限分别为 0.20μg/mL 和 0.50μg/mL）。

4　结语与展望

植物生长调节剂作为一种新型微毒农药，对环境以及人体健康的危害日益受到广泛研究和关注。考虑到植物生长调节剂双键、羧基等结构特性及其较高水溶性，以液液萃取或固相萃取为主的前处理技术以及以色谱-质谱联用法为主的分析测试技术在植物生长调节剂的分析测试中被广泛应用。但是，关于土壤和水体中痕量植物生长调节剂的分析测试问题仍亟待解决。未来，相关研究应聚焦于以下三个方面的内容。

（1）重视土壤和水体中痕量植物生长调节剂的分析测试

虽然现有以高效液相色谱-串联质谱法为主的分析测试技术，已经可以实现果树、肥料和营养液等环境基质中痕量植物生长调节剂的分析测试，但是土壤和水体中痕量植物生长调节剂的分析测试经常被忽视。在植物生长调节剂使用过程中，70%的植物生长调节剂在施用过程中会洒落于土壤表面，并可能通过吸收、传输进入到土壤或地下水中。同时，植物生长调节剂在土壤或地下水传输过程中伴随的一系列环境行为，使其含量呈递减趋势。因此，果树等农产品中植物生长调节剂的残留最为明显，而土壤中可能由于其高溶解度导致的快速迁移使其在土壤中的残留较少。另外，由于植物生长调节剂的自然衰减速度快，导致其在水体和土壤等复杂基质中的含量过低而无法进行检测。未来需进一步优化分析测试技术，特别是前处理方法，以更好地评估植物生长调节剂对土壤以及水体（特别是地下水）的环境风险。

（2）聚焦因环境行为产生的中间产物的分析测试

大多数植物生长调节剂都属于低毒或微毒，但一些植物生长调节剂在环境中降解的中间产物可能会有更大的毒性，如赤霉酸的水解产物异构赤霉酸及副产物赤霉烯酸和羟基赤霉酸等均有较强的毒性。目前，鲜有关于因环境行为产生的中间产物的研究，重视对不同环境介质中植物生长调节剂中间产物的定性、定量分析检测是未来的重点研究方向。

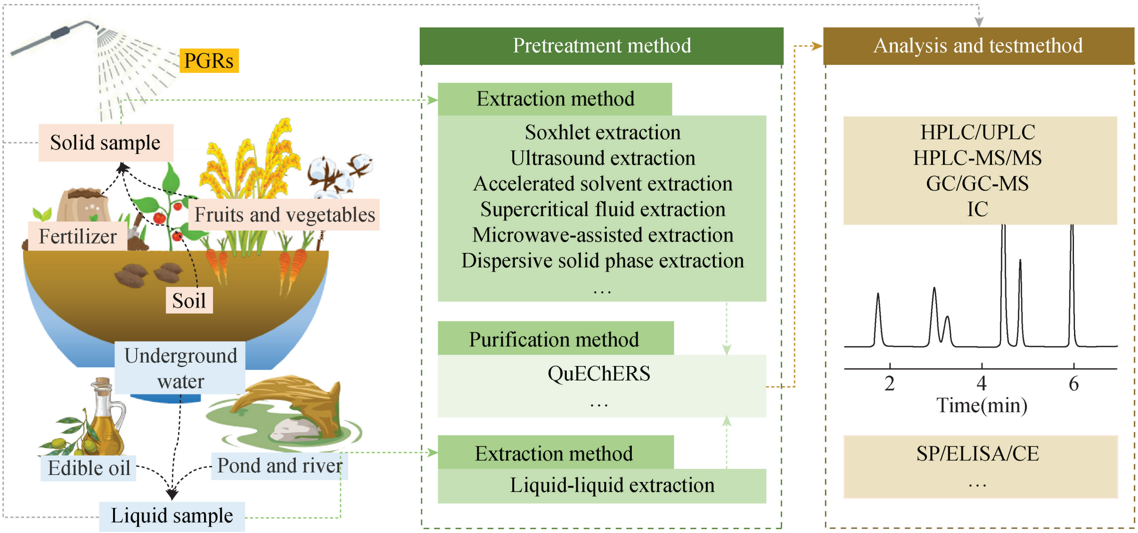
（3）开发基于新材料新技术的分析测试方法

色谱-质谱联用法的准确度高，检出限低，但仪器使用及维修费用高，普通基层实验室无法达到如此高的硬件条件，不利于现场及大量检测。一些成本低、效率高、耗时短的分析测试技术，如离子色谱法和微孔侧流免疫层析法，虽能进行日常快速检测和筛选，但无法满足土壤和地下水中植物生长调节剂微量残留的检测。未来需要开发的分析测试技术应当结合新材料或新技术，不断改进、研究新型便捷高效的检测方法，呈现多种技术交叉融合的新局面。

Review on the Analysis and Testing Method of Typical Plant Growth Regulators in Environment

HU Xiaolei[1,2], *CHEN Liang*[1,2*], *HOU Jie*[1,2], *WU Shaopei*[3], *WANG Lei*[3]

(1. State Key Laboratory of Hydraulic Engineering Simulation and Safety, Tianjin University, Tianjin 300350, China;
2. School of Civil Engineering, Tianjin University, Tianjin 300350, China;
3. Qiheng (Tianjin) Testing Technology Co., Ltd., Tianjin 300350, China)



HIGHLIGHTS

(1) The most widely used pretreatment methods for the detection of plant growth regulators are solid phase extraction or liquid-liquid extraction, and the most widely used purification technique is the QuEChERS method.

(2) The most widely used analytical test technique for plant growth regulators is high performance liquid chromatography-tandem mass spectrometry (HPLC-MS/MS), which could be used for the detection of plant growth regulators in different environmental media such as fruits, vegetables and fertilizers.

(3) Considering the quick natural attenuation ability of plant growth regulators and the higher toxicity of their intermediates, future research should focus on the analysis and test method of the trace plant growth regulators and its intermediates.

ABSTRACT

Plant growth regulators (PGRs) are defined as naturally occurring or artificially synthesized compounds. The functions of PGRs mainly include accelerating or delaying seed germination, breaking plant dormancy, stimulating or reducing bud elongation, inducing flowering and fruiting, and affecting the aging process. The application of PGRs has effectively promoted the growth of plants. However, the application concentration of PGRs is more than one millionth. The large amount of abuse and misuse of PGRs in the process of use not only reduces the yield of crops, but also exacerbates their residues in the environment, especially in agricultural products such as fruits and vegetables. So, they are detected in many environmental media like fruits, vegetables, and water. In addition, most PGRs are toxic, and some of them will undergo adsorption, desorption, hydrolysis, photolysis, microbial

degradation, and other environmental behaviors after entering the soil. The decomposition products produced by this process are more toxic. In order to comprehensively understand the current status of PGRs pretreatment, analysis and test method, the common pretreatment methods of solid phase extraction and liquid-liquid extraction for typical PGRs in solid substrates such as fruits and vegetables, fertilizers and soil, and in liquid substrates such as water, edible oil and nutrient solution are summarized in this paper, as well as the analysis and testing techniques such as high-performance liquid chromatography (HPLC) and ultra-high performance liquid chromatography (UPLC). Moreover, to reduce the detection limit, high-performance liquid chromatography-tandem mass spectrometry (HPLC-MS/MS) is also frequently used. At the same time, considering the strong natural attenuation ability of PGRs and the high toxicity of their intermediates, the advantages, disadvantages and applicability of different testing techniques are systematically summarized, taking into account the special structure and nature of PGRs, in order to fully understand the current status of pretreatment and analytical testing of PGRs and provide literature support for subsequent research on analytical testing, migration transformation, pollution evaluation and treatment of PGRs.

Due to many impurities in the sample that can interfere with the detection, the appropriate pretreatment method can improve the accuracy of the test results. However, the sample pretreatment process accounts for more than 70% of the total analysis and test work, and about 50% of the error in the final test results comes from pretreatment. Therefore, establishing a fast, simple, and stable pretreatment method can effectively improve the efficiency and accuracy of analysis and detection. At present, the forms of environmental media detected for PGRs are mainly divided into two types: solid matrix samples (such as fruits, vegetables, fertilizers and soil, etc.) and liquid matrix samples (water, oil and nutrient solution, etc.). The related pretreatment methods are also mostly targeted at these two different forms of environmental media.

Solid substrates involving PGRs mainly include fruits and vegetables, fertilizers and soil. Among them, fruits and vegetables are the most frequently detected solid substrates of PGRs, and some PGRs have also been detected in fertilizers, soil and other substrates. The pretreatment process of solid matrix samples can be divided into two parts: extraction and purification. Among them, solid phase extraction is the most commonly used extraction technology, and QuEChERS method is the most widely used purification method.

Water, edible oil, and nutrient solution are the most frequently detected liquid substrates of PGRs. At present, liquid-liquid extraction is the most commonly used extraction method for liquid matrix. For the selection of extractants, the octanol-water partition coefficient of PGRs such as gibberellic acid and ethephon is less than 1, which is a strong polar compound and can be extracted by hydrophilic organic solvents such as methanol, ethanol and acetone; the polarity of most other PGRs such as forchlorfenuron and paclobutrazol is relatively weak, but it still belongs to the category of strong polarity compared with other kinds of compounds such as benzene and chloroethane (*n*-octanol-water partition coefficient>10). Therefore, the extractant can not only use methanol, but also use polar organic solvents such as ethyl acetate and chloroform that are insoluble in water. Although liquid-liquid extraction requires a lot of extractants, the high-water solubility of most PGRs makes them often directly detected by HPLC-MS/MS, which eliminates the complex pretreatment steps such as extraction and purification. In addition, because some PGRs have poor chromatographic characteristics or are not easily detected, the derivatization is also required to convert the components into derivatives suitable for analysis.

Analytical and testing technologies mainly include gas chromatography (GC), gas chromatography-mass spectrometry (GC-MS), HPLC/UPLC, HPLC-MS/MS, ion chromatography (IC), spectrophotometry (SP), capillary electrophoresis (CE), enzyme-linked immunosorbent assay (ELISA) and electrochemical sensor method.

At present, the solubility of most PGRs in water (20℃) is 0.50-10g/L, and the octanol-water partition coefficient of most PGRs is 0-4, with strong hydrophilicity. Therefore, HPLC-MS/MS are applicable to the

detection of almost all PGRs. However, HPLC-MS/MS are often used to detect the residues of PGRs in fruits and vegetables, followed by soil and fertilizer, while there are few related studies in natural water. This may be due to the rapid natural decay rate of PGRs in the natural environment, resulting in extremely small amounts of residues in natural water bodies such as surface water and groundwater that cannot be directly detected.

GC has the advantages of low cost and easy maintenance, and GC-MS has become a conventional testing technology. However, GC-MS are greatly affected by sample matrix interference and require high pretreatment methods. In addition, due to the influence of the physical and chemical properties of different PGRs (such as abscisic acid and indole acetic acid with a boiling point over 400℃, or forchlorfenuron and cinnamic acid with hydroxyl and carboxyl groups), most PGRs have poor gas chromatographic characteristics and are not easily detected.

The order of detection limits of PGRs is GC > HPLC > chromatography-mass spectrometry, and the lowest instrumental detection limit of chromatography-mass spectrometry is 10^{-5}mg/kg. However, the higher solubility and the larger natural attenuation rate of most PGRs lead to the lower detection concentrations in complex environmental substrates such as soil and water, so there is still an urgent need to solve the problem of analytical testing of trace PGRs and its intermediates.

In future, PGRs analysis and test method will focus on the analysis and detection of trace PGRs and their intermediates, as well as the development of new materials and technology-based methodologies.

KEY WORDS: plant growth regulators; solid phase extraction; liquid-liquid extraction; high performance liquid chromatography; chromatography-mass spectrometry; detection limit

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