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水环境中新污染物快速检测技术研究进展

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摘要: 国内外广泛关注的新污染物主要包括抗生素、内分泌干扰物、全氟或多氟化合物等污染物质, 这些污染物通过径流、扩散、渗透等多种途径进入水体环境。由于新污染物多具有生物累积性、生物毒性及环境持久性等特征, 对水生生物、人体健康和生态安全构成潜在威胁, 存在环境风险, 因此, 国家对其污染现状开始进行调查。随着中国新污染物污染状况调查评价工作的开展, 快速、灵敏的检测方法成为研究热点。本文基于近年文献重点评述了水环境中新污染物的检测方法, 并对方法的性能和优缺点作了对比。结果表明: ①目前新污染物的检测方法以大型仪器检测方法为主。仪器检测方法的检测浓度低、精度高, 对设备的要求高, 从采样到测试分析得到结果的周期长, 不适用于新污染物的现场快速检测。②传感检测技术和免疫分析技术逐步应用于新污染物的快速检测。其中电化学传感器和酶联免疫分析法相对成熟, 应用较多, 具有设备简单、检测时间短, 灵敏度和精确度良好等优点, 可开展现场快速检测。本文认为, ①快速检测技术多针对单一污染物进行检测, 而实现同时检测多种污染物质还需进一步研究; ②多种检测技术相结合可以达到更好的检测效果, 是未来新污染物检测的发展方向; ③利用新型材料改良检测方法、降低检出限、提高灵敏度和精确度实现新污染物快速检测是未来研究的难点和重点。

关键词: 新污染物; 快速检测; 仪器分析; 传感器; 免疫分析

要点:

- (1) 新污染物的仪器检测分析周期长、成本高, 对快速检测方法需求越来越大。
- (2) 传感器检测技术与免疫分析检测技术是目前常用的新污染物快速检测技术。
- (3) 多种检测技术结合以实现高效灵敏的快速检测新污染物是未来发展方向。

中图分类号: X832; X52

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生态环境部于2021年10月发布《新污染物治理行动方案(征求意见稿)》, 其中定义新污染物是指新近发现或被关注, 对生态环境或人体健康存在风险, 尚未纳入管理或者现有管理措施不足以有效防控其风险的污染物。目前, 国内外广泛关注的新污染物主要包括抗生素、内分泌干扰物、全氟或多氟化合物等。水是新污染物的主要载体, 新污染物在水

循环系统中, 通过径流、扩散、渗透等多种途径进入地表水和地下水。由于新污染物多具有生物毒性、环境持久性、生物累积性等特征, 即使新污染物在水体中浓度较低, 也可能具有显著的环境与健康风险, 对水生生物、生态安全和人体健康构成潜在威胁^[1]。因此, 对于水环境中新污染物污染状况的检测调查迫在眉睫。

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水环境中的新污染物检出率高,含量低。抗生素是国内外水体中检出最普遍的新污染物。前人调查结果显示黑龙江省哈尔滨市地下水中 6 大类典型抗生素均有不同程度地检出^[2]。河北省石家庄市地下水中共检出 13 种喹诺酮类抗生素,部分种类检出率高达 100%^[3]。地表河流如滏阳河与沁河均有抗生素检出^[4]。湖北省宜昌市与沱江流域水源水中也有部分抗生素检出^[5-6]。中国地下水抗生素的检出浓度在 0.1~1000ng/L 之间^[7]。巴基斯坦地下水中主要存在替加环素和环丙沙星,平均浓度分别为 21.3ng/L 和 18.2ng/L^[8]。环境中检出内分泌干扰物的检出率高,浓度在 ng/L 甚至 $\mu\text{g/L}$ 级。江苏省无锡—常州地区地下水中有 20 种内分泌干扰物被检出,检出率均在 90% 以上^[9]。徐州地区地下水含有双酚 A,且最高值达 26.45ng/L^[10]。闽江流域水体中有酚类内分泌干扰物检出,浓度范围在未检出至 1.06 $\mu\text{g/L}$ 之间,检出率在 55.88%~100.00% 之间^[11]。罗马尼亚黑海沿岸海水中有部分内分泌干扰物被检出,浓度最高达 5.6 $\mu\text{g/L}$,对海洋生物存在中高风险^[12]。环境中的全氟化合物是随着测试技术的发展走进人们的视野的,虽然在全球范围内已经停止使用,但是由于其具有比较稳定的物理化学性质以及环境持久性,仍然有较高的检出率。北京市再生地下水灌区中不同程度地检出包括全氟羧酸和全氟磺酸在内的 10 种全氟多氟化合物^[13]。海南省部分区域农田地下水环境中存在全氟烷基酸污染,总量在 0.85~49.62ng/L^[14]。洪泽湖表层水中检出 15 种全氟化合物^[15]。在印度南部河流中有 12 种全氟化合物被检出^[16]。由此可见,国内外水环境中均存在新污染物污染现象,且部分地区污染浓度和检出率较高,存在风险。

国务院于 2022 年 5 月 24 日发布的《关于新污染物治理行动方案的通知》中指出依托现有生态环境监测网络,在重点地区、重点行业、典型工业园区开展新污染物环境调查监测试点;探索建立新污染物环境调查、监测及健康风险评估技术方法。随着中国新污染物污染状况调查评价工作的开展,快速、灵敏的检测方法成为研究热点。目前国内外新污染物检测的技术主要有仪器检测技术、传感检测技术和免疫检测技术等。其中仪器检测技术最为成熟,使用范围广,对新污染物检测的精密度高、检出限低且方法稳定,但是对新污染物的前处理比较复杂、检测时间长,并且仪器设备多为大型仪器,单价较高、对应用人员也有要求,非一般实验室能够承受,不适

用于野外现场快速测定水样中新污染物。传感检测技术和免疫分析技术具有设备简单、检测时间短、灵敏度和精确度良好等优点,逐步应用于新污染物的现场快速检测。其中电化学传感器和酶联免疫分析法相对成熟,应用较多。本文总结了水环境中新污染物现场快速检测技术领域的相关研究工作,旨在为新污染物的监测和评估技术的发展提供有益的技术支持。

1 仪器检测技术

仪器检测技术是指利用大型仪器设备来对特定目标物质进行分析的技术。新污染物在水环境中虽然检出率高,但是检出浓度非常低,含量在 $\mu\text{g/L}$ 和 ng/L 级,利用高倍数浓缩前处理,并采用高分辨率的大型仪器设备分析是目前水环境中新污染物主要的检测方法。

1.1 抗生素检测方法

抗生素的检测方法主要有毛细管电泳、高效液相色谱法(LC)、液相色谱-质谱联用法(LC-MS)、高效液相色谱-串联质谱法(HPLC-MS/MS)、超高效液相色谱-串联质谱法(UPLC-MS/MS)等,可检测抗生素种类主要有磺胺类、喹诺酮类、大环内酯类、四环素类和氯霉素类等。毛细管电泳的检出限可以达到 $\mu\text{g/L}$ 级,能够满足对地表水体中抗生素的检测。地下水抗生素虽然检出比较普遍,但是浓度一般偏低,因此需要更低的检出限。除毛细管电泳法以外,其他方法均能达到 ng/L 级,可用于地下水中抗生素的检测,其中 HPLC-MS/MS 法是目前应用较为广泛的抗生素定量分析方法,具体性能见表 1。

1.2 内分泌干扰物检测方法

环境内分泌干扰物在水环境中广泛存在,但含量极低,通常为 $\mu\text{g/L}$ 甚至 ng/L 级。近年来,各种高效、快速的样品预处理技术及检测技术已广泛应用于水环境中内分泌干扰物的研究。目前,内分泌干扰物的检测方法主要有气相色谱-质谱联用法(GC-MS)、高效液相色谱法、LC-MS 法、HPLC-MS/MS 法、UPLC-MS/MS 法等,可检测内分泌干扰物以酚类和雌激素类为主,环境中的内分泌干扰物检出率高但浓度极低,HPLC-MS/MS 检出限可以达到纳克级别,可应用在水环境中痕量内分泌干扰物的检测,具体性能见表 2。

1.3 全氟化合物检测方法

早在 1968 年科学家已经在人体血浆中发现有机氟化物的存在,直到二十世纪九十年代中后期液相色谱和质谱分析仪器的的发展,全氟化合物的测试

才有可能到纳克级,才第一次允许科学家们研究生物和环境要素中全氟化合物的背景值^[45]。目前,全氟化合物的检测方法主要有GC-MS法、LC-MS法、HPLC-MS/MS法、UPLC-MS/MS法等,可检测全氟化合物有全氟烷基化合物、全氟羧酸化合物等。HPLC-MS/MS法用于检测全氟化合物的研究较多,检出限低至0.01ng/L,可用来检测水环境中痕量的全氟化合物,具体性能见表3。

仪器检测技术具有高通量、准确度高、检出限低、假阳性率低等优点,但是需要对样品进行高要求的前处理,并且对设备的要求高,从采样到测试分析得到结果的周期长,只能在实验室进行操作,无法满足水环境中新污染物的现场快速检测的需求。仪器

检测技术的发展方向主要有两个:一是样品的前处理将向着绿色环保、高效、小型便携化和自动化等方向发展;二是样品的仪器分析朝着快速检测、高选择性、高灵敏等方向发展^[57]。

2 现场快速检测技术

快速检测是指可以快速、灵敏地检测出目标污染物,并且操作简单的检测技术^[58]。目前针对新污染物的快速检测方法有利用传感器检测原理的传感检测技术、基于生物检测原理的免疫检测技术以及其他多种检测方法相结合的检测技术,其中,传感检测以电化学传感为主,免疫检测以免疫分析为主,可应用于水环境中新污染物的现场快速检测。

表1 仪器检测技术可检测抗生素种类及其性能

Table 1 The antibiotics types and performance of instrument detection technology that can be detected.

检测方法	仪器设备	可检测抗生素种类	检出限	RSD(%)	参考文献
毛细管电泳(CE)	高效毛细管电泳仪	磺胺类、喹诺酮类、四环素类等	0.4 ~ 1.0μg/L	-	[17-18]
高效液相色谱法(HPLC)	高效液相色谱-串联质谱仪	磺胺类、喹诺酮类、大环内酯类、四环素类、氯霉素类等七大类	0.06 ~ 2.28ng/L	-	[19]
	高效液相色谱-串联紫外/荧光检测器	磺胺类、喹诺酮类、氯霉素类等	4.2 ~ 22.8μg/L	-	[20]
液相色谱-质谱联用法(LC-MS)	液相色谱-串联质谱仪	磺胺类、喹诺酮类、大环内酯类、四环素类等	0.15 ~ 0.9ng/L	0.36 ~ 2.25	[21-22]
	液相色谱仪;三重四极杆质谱仪	磺胺类、喹诺酮类、大环内酯类、四环素类等	1.2 ~ 15ng/L	<22	[23]
高效液相色谱-串联质谱法(HPLC-MS/MS)	三重四级杆质谱仪;高效液相色谱仪	磺胺类、喹诺酮类、大环内酯类、头孢霉素类等	0.0056 ~ 3.9675ng/L	<11	[24-25]
	高效液相色谱-串联质谱仪	喹诺酮类	0.1μg/L	0.71 ~ 12.80	[26]
超高效液相色谱-串联质谱法(UPLC-MS/MS)	超高效液相色谱仪;三重四极杆质谱仪	磺胺类、喹诺酮类、大环内酯类、四环素类、氯霉素类等七大类	0.01 ~ 10.6ng/L	≤16	[27-30]

表2 仪器检测技术可检测内分泌干扰物种类及其性能

Table 2 The environmental endocrine disruptors types and performance of instrument detection technology that can be detected.

检测方法	仪器设备	可检测内分泌干扰物种类	检出限	RSD(%)	参考文献
气相色谱-质谱联用法(GC-MS)	气相色谱-质谱仪	类固醇类、酚类等	0.5 ~ 140ng/L	2.54 ~ 5.36	[31]
高效液相色谱法(HPLC)	高效液相色谱仪-串联荧光检测器	三氯生、β-雌二醇、壬基酚和4-辛基酚	1.1 ~ 1.9ng/L	-	[32-33]
	高效液相色谱仪	邻苯二甲酸二丁(辛)酯	0.1μg/L	<4.47	[34]
高效液相色谱-串联质谱法(HPLC-MS/MS)	高效液相色谱仪-串联二极管阵列检测器	三氯生、三氯卡班和甲基三氯生	0.05 ~ 0.2μg/L	<10	[35]
	高效液相色谱仪;质谱仪	对乙酰氨基酚等17种	0.07 ~ 1.88ng/L	-	[36]
超高效液相色谱-串联质谱法(UPLC-MS/MS)	高效液相色谱系统;三重四极杆质谱仪	黄体酮代谢物、类固醇类、酚类等	0.02 ~ 50ng/L	<15	[37-39]
	超高效液相色谱-串联质谱仪	雌激素类、雄激素类、肾上腺皮质激素类、酚类和非甾类激素类等	0.05 ~ 2.00ng/L	0.99 ~ 12.0	[40-41]
	超高效液相色谱系统;三重四极杆质谱仪	酚类、黄体酮等	0.03ng/L ~ 5.0μg/L	≤11.6	[42-44]

表 3 仪器检测技术可检测全氟化合物种类及其性能

Table 3 The perfluorinated and polyfluoroalkyl substances types and performance of instrument detection technology that can be detected.

检测方法	仪器设备	可检测全氟化合物种类	检出限	RSD(%)	参考文献
气相色谱-质谱联用法 (GC-MS)	气相色谱-质谱仪	中性全氟烷基化合物、全氟羧酸化合物等	0.02ng/L ~ 1.5μg/L	< 14.5	[46-47]
液相色谱-质谱联用法 (LC-MS/MS)	液相色谱仪; 三重四极杆质谱仪	全氟辛烷磺酸等 22 种以上全氟烷基化合物	0.16 ~ 5.13ng/L	3 ~ 18	[48-49]
高效液相色谱-串联质谱法 (HPLC-MS/MS)	高效液相色谱仪; 质谱仪	全氟辛烷磺酸等 21 种全氟化合物	0.01 ~ 0.08ng/L	1.1 ~ 11.2	[50]
超高效液相色谱-串联质谱法 (UPLC-MS/MS)	超高效液相色谱-串联四极杆质谱仪	全氟羧酸、全氟磺酸、全氟醚羧酸等 57 种以上全氟化合物	0.01ng/L ~ 0.1μg/L	0.4 ~ 23.0	[51-53]
	超高效液相色谱-质谱仪	全氟丁烷磺酸、全氟辛酸和全氟辛烷磺酸等 16 种以上全氟化合物	0.06ng/L ~ 0.25μg/L	2.1 ~ 9.19	[54-56]

2.1 传感检测技术

传感检测是利用传感器来检测污染物质的技术, 传感器通过敏感元件及转换元件将特定的被测物质, 按照一定规律转换成某种可用信号并输出显示, 以此来获得所需信息^[59], 检测原理见图 1。传感检测技术是环境监测领域常用野外现场检测方法, 主要有电化学传感、光学传感和生物传感等, 在水环境中新污染物的现场快速检测方面有很大的发展前景。

2.1.1 电化学传感器

电化学传感检测依赖传感器上的敏感元件与被测溶液建立的线性关系产生可识别电信号, 从而确定目标物的含量, 由于不同目标物的氧化还原电位不同, 因此电化学传感器可以定性定量地识别不同的目标物^[60]。目前, 电化学传感器多用于传统污染物的检测, 如金属离子、酚类化合物、多环芳烃等, 新污染物中抗生素基本骨架及衍生官能团决定了不同抗生素具有不同的电化学活性, 因此目前电化学传感器研究最多是抗生素的检测, 针对内分泌干扰物和全氟化合物的研究较少。

利用不同材料修饰电极, 用以优化电化学传感器, 是常用的研究方法。黄鹏程等^[61]利用 TiO₂/聚乙烯醇 (PVA) 纳米复合材料修饰电化学检测技术,

对雨水样品中的四环素类抗生素进行检测, 证明了 TiO₂/PVA 纳米复合物对抗生素的检测具有较高的重复性和响应性。王群等^[62]研究了 Ag/CMC@TiO₂/LIG、β-CD/SmO_x NPs/LIG 两种电化学传感器, 通过实验证明都可以应用到实际水样中抗生素 (氯霉素和氧氟沙星) 的检测 (RSD < 7.1%)。孙心悦^[63]利用钨/二氧化钛-还原氧化石墨烯作为电极材料制备了可以重复检测水中的内分泌干扰物 (如双酚 A) 的可更新传感器, 并且有一定的抗干扰能力。同样, Verma 等^[64]利用还原氧化石墨烯和三氧化钼纳米颗粒纳米复合材料, 开发了一种非常高效、敏感的电化学传感器用来检测水环境中内分泌干扰物。

分子印迹聚合物是常见的电极修饰材料, 可进一步改良电化学传感器的灵敏度和精确度。孙俊永等^[65]制备了一种对磺胺类抗生素具有高识别性能的分 子印迹聚合物来修饰电化学传感器, 可实现对磺胺类抗生素的高灵敏同时测定。王孟龙等^[66]基于分子印迹技术建立的电化学传感检测平台证明了该技术检测内分泌干扰物的可行性。金属有机框架同样可用来修饰电极, 雷小玲^[67]利用导电金属有机框架与分子印迹聚离子液体复合材料, 构建了一种检测内分泌干扰物的电化学传感器, 检测性能更加优越, 且有很好的选择性。

除此之外, Cheng 等^[68]利用一种多孔吸附剂探针, 通过将其嵌入微流体平台来提高检测的灵敏度 (检出限 0.5ng/L), 建立了一种可用于快速检测全氟辛烷磺酸的电化学传感器平台。

2.1.2 光学传感器

光学传感是基于光学原理利用传感器将光学信号转化成可识别信号并显示出来, 从而实现对目标

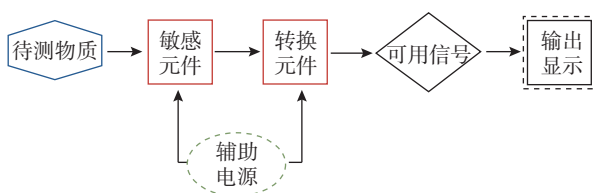


图1 传感器检测原理示意图

Fig. 1 Principle diagram of sensor detection.

物质的检测。光学传感器类型多样,普遍具有操作简单、检出限低、灵敏度高、耗时短等特点,可应用于水环境中新污染物的检测,目前多应用于抗生素类污染物的检测,针对部分内分泌干扰物和全氟化合物也有少量研究。

光学传感类型包括表面增强拉曼光谱(SERS)、表面等离子体共振(SPR)和荧光探针等。马海宽等^[69]利用SERS和静电富集相结合的技术,实现了水环境中抗生素类的有效富集和快速痕量探测。Gao等^[70]将掺杂 $Zn_{1-x}Ce_xO$ 半导体衬底的SERS应用于内分泌干扰物(双酚A)的痕量检测,可实现在1min内超灵敏检测(检出限 $<0.1\mu\text{g/L}$)。李晶等^[71]基于氟-氟相互作用的上转换荧光法构建了一种可以实现对水环境中痕量全氟化合物(如全氟辛酸磺酸)快速测定的荧光探针。Sullivan等^[72]利用固相分子印迹技术合成了靶向抗生素类高亲和纳米颗粒,结合SPR传感器,可以实现对水中特异性和低水平的喹诺酮类抗生素的检测。光学传感与电化学传感结合,可弥补电化学传感器电极易被污染的缺点,基于此,Hu等^[73]利用ZIF-8电极在光照下可在短时间内实现连续重复试验的自清洁和再生性能,构建了一种多孔ZIF-8光电化学传感器,可稳定、灵敏地检测磺胺类抗生素和双酚A(RSD $<5.9\%$),但是检出限较高,无法直接检测到实际水样中污染物。

2.1.3 生物传感器

生物传感器是一种以生物分子为识别元件,与信号转换元件反应后通过信号转换器转换为可测量信号的分析设备,以此来对目标物进行定性或定量分析^[74]。生物传感器具有高特异性、高灵敏度、快速、可适用现场检测等优势,被广泛应用于环境监测领域,但针对环境中新污染物的应用较少。

光纤生物传感器和核酸适配体传感器是两种较为常用的生物传感器。基于免疫分析原理改进光纤生物传感器,可优化生物传感器的性能。卓雨欣等^[75]基于间接竞争免疫分析原理,利用倏逝波光

纤生物传感平台研发了一种抗生素检测方法,能够用于实际水样中抗生素(如诺氟沙星)的快速检测。Cennamo等^[76]基于酶联免疫分析原理,提出一种新型表面等离子体共振光纤生物传感器,可应用于海水样品中全氟辛酸和全氟辛酸磺酸的检测,检出限低至 $0.21\mu\text{g/L}$ 。核酸适配体^[77-78]具有稳定性高、特异性强、易于合成和修饰、适应范围广等优点,适配体传感器已经被应用于重金属、小分子和蛋白质等多种物质的检测,逐渐应用在环境新污染物的检测中。刘晓等^[79]建立一种可在30min内完成定量检测雌二醇的荧光适配体传感器。Yang等^[80]开发了一种可重复使用的光纤化学发光适配体生物传感器,在15min内完成了内分泌干扰物检测。

2.1.4 传感检测技术优缺点

目前,基于电化学传感的检测方法研究较多,传感检测技术可实现对水中传统污染物的快速检测,对新污染物的相关研究相对较少,并且多针对单一污染物质进行检测,研究多存在于实验室阶段,或者无法直接检测实际水样,应用于水环境中新污染物的现场快速检测实例更少,且对实际水样中多种污染物质无法做到同步检测。表4总结了水环境中新污染物传感检测技术的优缺点。

2.2 免疫检测技术

免疫检测技术,是指基于抗原抗体特异性结合原理的免疫分析检测技术,检测原理见图2。免疫检测技术操作简单、用时短、无需昂贵仪器设备,适合水环境中新污染物的现场快速筛查,包括免疫分析法(ISA)和免疫层析法(ICA)等。

2.2.1 免疫分析法

酶联免疫分析法(ELISA)通过显色反应的深浅来定性或定量分析目标污染物,是环境监测中应用较多的一种免疫分析方法。该检测技术的检出限低、灵敏度、准确度和精密度都良好,可应用于新污染物污染情况的初步筛查。马建国^[81]利用间接竞争ELISA证明了该技术可应用于检测水样中的磺胺类

表4 水中新污染物传感检测技术优缺点对比

Table 4 Comparison of advantages and disadvantages of emerging contaminants sensor detection methods for water samples.

传感检测技术	优点	缺点
电化学传感	操作简单,成本低廉,分析速度快,仪器体积小,易携带,适用于现场检测	检出限较高,电极构造耗时、繁琐,电极易被污染,需定期更换电极
光学传感	操作简单,成本低,可实时检测	灵敏度一般,容易受环境干扰,使用寿命较短,大多只能对特定污染物进行检测
生物传感	操作简单,费用低,适用于批量样品快速筛选	易受到水样中其他物质干扰,专一性和精确度不足

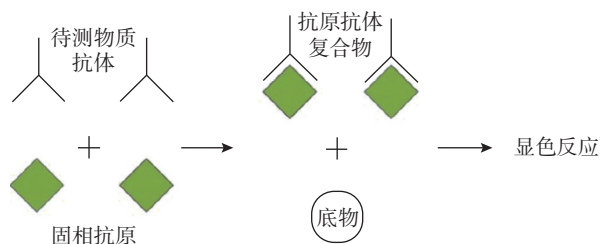


图2 免疫检测原理示意图

Fig. 2 Principle diagram of immunoassay detection.

抗生素、磺胺类的检出限为 2.64ng/L, 检测结果良好。张玉超等^[82]建立了一种基于单克隆抗体的双酚 A 间接竞争酶联免疫分析方法, 实验结果证明该检测方法可以应用于水样中双酚 A 的快速检测。贾文哲等^[83]将间接 ELISA 反应条件优化后实现对两种内分泌干扰物(雌二醇、壬基酚)的同时检测, 检出限分别为 3.18 μ g/L 和 24.78 μ g/L。朱江等^[84]利用基于全氟辛烷磺酸多克隆抗体的 ELISA 检测了水样中全氟辛烷磺酸残留, 证明 ELISA 可用于水样中 PFOS 的检测。此外, 链式免疫分析法 (ULISA) 也是一种可应用于新污染物的免疫检测方法, Wang 等^[85]利用 808nm 激发上转换纳米颗粒结合亲和素-生物素复合物原理, 采用 96 孔酶联板作为检测平台, 满足高通量需求, 建立了一种可同时检测 3 种抗生素的免疫检测方法, 检出限分别为磺胺甲基嘧啶 0.15 μ g/L、沙拉沙星 0.03 μ g/L、四环素 0.05 μ g/L, 可实现设备小型化, 有望实现现场化。

2.2.2 免疫层析法

免疫层析法以试纸条为载体, 利用抗原抗体反应, 不同浓度的目标物会产生不同的反应结果, 从而得到目标物的定性或定量结果^[86]。免疫层析法更多地应用在食品和医药行业, 而用于水中新污染物检测的研究很少, 常用的标记材料有胶体金、量子点、上转换材料和荧光微球等。早在 2007 年杜志辉等^[87]就制备出一种能够对环境样品中壬基酚进行快速检测的胶体金免疫试纸条, 能够在 10min 内对样品检测完毕, 且操作简单, 能够实现对壬基酚污染事故的快速定性检测, 该试纸条的检测限为 4.4 \pm 2.5ng/L, 但仍需改进。Pu 等^[88]以金纳米粒子为比色探针, 建立了一种灵敏度高、选择性好的内分泌干扰物检测方法 (RSD 为 3.4%~8.9%), 可用于实际水样中雌二醇的现场快速测定。

2.2.3 免疫检测技术优缺点

应用免疫检测技术用于测定水中的新污染物, 可以达到现场快速检测的目的, 并且根据对实际水

样的检测, 检出限达到微克级, 可以对水中新污染物进行初步快速筛查。免疫检测技术特异性高、敏感性强, 简单方便、无需昂贵仪器设备, 在大量样品及现场快速检测方面具有极大的优势, 但是容易出现假阴性和假阳性^[89]。

2.3 其他检测技术

除了传感检测技术和免疫检测技术, 已有学者将几种检测方法结合, 针对具体某一新污染物进行快速检测, 实现对原有检测技术的改良, 以此来降低检出限、缩短检测时间、提高灵敏度及准确度。

将传感技术与免疫分析原理结合, 是学者们研究较多的一种新污染物快速检测的方法。平面波导免疫传感器将间接免疫反应原理与传感技术结合, 能够实现对新污染物快速、灵敏的检测, 可以对几种物质同时进行检测。贾文哲^[90]利用平面波导免疫传感器, 研究建立了针对内分泌干扰物的生物传感器检测方法, 对实际水样进行检测实验后证明该传感器的精密度及准确度良好, 并且可以重复使用, 节约成本, 也保证了免疫传感器检测的稳定性。徐玮琦等^[91]基于平面波导型全内反射荧光生物传感器, 建立了一种可以快速、高灵敏检测环境中痕量内分泌干扰物(如双酚 A)的方法。李树莹等^[92]基于间接竞争免疫反应及荧光全内反射原理, 以平面波导生物传感器为平台, 建立了针对抗生素(恩诺沙星和诺氟沙星)的同时快速检测方法(检测限为 0.06 μ g/L), 检测周期仅 15min。单迪迪等^[93]基于阵列倏逝波荧光传感器, 运用间接竞争免疫检测模式, 优化检测条件后, 可用于实际水体中内分泌干扰物(如雌二醇)的快速检测。

此外, 其他学者研究的检测方法也为快速检测新污染物提供了新思路。高燕梅等^[94]建立了一种使用单扫描极谱检测体系中盐酸小檗碱的峰电流从而间接检测全氟辛烷磺酸的新方法。王硕等^[95]利用合成的雌酮分子印迹聚合物作为微柱填料, 建立了一种原位显色反应的方法, 通过对实际水样中的痕量雌酮的检测分析, 发现有很明显的显色反应, 证明了该技术的可行性。He 等^[96]开发了一种共振瑞利散射-比色双通道传感器用于全氟辛烷磺酸的检测, 包括混合和检测在内的整个方法用时小于 8min, 可应用于实际水样的检测。多种技术相结合, 可以达到更好的检测效果, 是未来快速检测新污染物的发展方向。

2.4 现场快速检测技术现状

随着新污染物研究的开展, 现场快速检测技术

作为仪器检测技术的一种补充将有越来越大的需求。传感检测技术相对成熟,应用于快速检测水环境中一般污染物,能够实现对部分抗生素、内分泌干扰物和全氟化合物的快速定量检测,其中电化学传感研究最多,其次为光学传感。免疫检测技术应用在环境检测领域以免疫分析为主,酶联免疫分析法可初

步筛查水中新污染物的污染状况,免疫层析法可对新污染物进行定性或半定量检测。除此之外,也有学者利用其他方法针对某一具体的新污染物进行快速定量检测,这些方法具有针对性,能够降低检出限,但检测目标单一。表5对文献中涉及的现场快速检测方法可检测新污染物类别进行了总结。

表5 不同类别新污染物可选择的快速检测方法总结

Table 5 Summary of emerging contaminants that can be detected by rapid detection methods.

快速检测技术分类	方法名称	抗生素类	全氟化合物类	内分泌干扰物类
传感检测技术	电化学传感	√	√	√
	光学传感	√	√	√
	生物传感	√	√	√
免疫检测技术	酶联免疫分析法	√	√	√
	免疫层析法	-	-	√
其他快速检测技术	平面波导免疫传感器	√	-	√
	荧光免疫生物传感器	-	-	√
	阵列倏逝波荧光传感器	-	-	√
	单扫描极谱	-	√	-
	原位显色反应	-	-	√

注:“-”表示该类新污染物不涉及。

3 总结与展望

检测水环境中新污染物常用的方法为仪器检测,然而大型仪器虽然灵敏度高、检出限低,但是存在检测周期长、设备昂贵、对操作人员要求高等缺点,并且不能用于野外现场检测。传感器检测和免疫检测由于其设备简单、检测时间短、灵敏度和精确度良好,逐渐应用于水环境中新污染物的快速以及现场检测,常用的快速检测方法有电化学传感器和酶联免疫分析法,检出限可低至纳克级,可以满足大部分水环境中新污染物的检测,并且足够稳定,成本低。

新污染物的快速检测方法类型多样,但大多只

针对单一污染物进行检测,实现同时检测多种污染物物质还需进一步研究,已有的报道多是实验室阶段,是否真正可以应用于实际样品的检测还有待检验。在传统方法的基础上,利用新型材料改良检测方法,降低检出限,提高灵敏度和精确度,使其达到新污染物检测的需求,进一步应用于实际样品的现场快速检测,是现在以及未来研究的重点。将多种检测技术相结合,使检测方法更加简单、快速、成本低,并且灵敏度和精确度都足够高,能够同时对多种污染物实现现场快速检测,是未来研究的方向。

A Review of Rapid Detections for Emerging Contaminants in Groundwater

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HIGHLIGHTS

- (1) Due to the long cycle and high cost of instrument detection technologies for emerging contaminants, rapid detection technology is needed.
- (2) Sensor detection technology and immunoassay detection technology are commonly used for rapid detection of emerging contaminants.
- (3) The development direction of rapid detection of new pollutants in the future is to combine multiple detection technologies with high efficiency and sensitivity.

ABSTRACT: In recent years, emerging contaminants, such as antibiotics, endocrine disruptors, perfluorinated and polyfluoroalkyl substances, are of great worldwide concern. These contaminants enter the water environment through runoff, diffusion, infiltration and other ways. Due to their bioaccumulation, biological toxicity, and environmental sustainability, emerging contaminants pose a potential threat to aquatic organisms, human health, and ecological safety^[1]. Therefore, it is urgent to detect and investigate the pollution status of emerging contaminants in the water environment. Many investigations and evaluations have been carried out, making rapid detection methods a research hotspot. The detection methods of emerging contaminants in the water environment based on recent literature is reviewed, comparing the advantages and disadvantages of the emerging contaminants detection methods, summarizing the research progress of rapid detection technology for emerging contaminants in water, and prospecting its development trend.

Emerging contaminants were widely detected in the water environment. For instance, antibiotics have been detected in groundwater in cities such as Harbin^[2] and Shijiazhuang^[3], in surface rivers such as the Fuyang River and Qin River^[4], and in the source water such as Yichang City^[5] and the Tuojiang River Basin^[6], as well as in groundwater from major urban-rural settings of Pakistan^[8]. Similarly, endocrine disruptors have been detected in different types of water in China, such as the Minjiang River Basin^[11], as well as in groundwater of the Wuxi—Changzhou region^[9] and Xuzhou region^[10]. Some endocrine disruptor pollutants have been detected in seawater along the Romanian Black Sea coast^[12]. In addition, perfluorinated and polyfluoroalkyl substances have been detected in the surface water of Beijing's reclaimed groundwater irrigation area^[13] and in Hongze Lake^[15]. There is perfluoroalkyl acid pollution in the groundwater environment of farmland in some regions of Hainan Province^[14]. Perfluorinated compounds have also been detected in major Southern Indian rivers^[16]. There are emerging contaminants in the water environment both domestically and internationally. The concentrations and detection rates are high in some areas, posing a serious threat to groundwater and surface water resources.

Nowadays, the emerging contaminants are mainly detected in the laboratory using advanced instruments. The emerging contaminants are widely present in the environment, but their concentrations are quite low, of which the content is in the nanogram to microgram level. In order to reduce the detection limits, the emerging contaminants samples will be concentrated and then tested using high-resolution instruments. Instrument detection technology has the advantages of high throughput, high accuracy, low detection limit, and low false positive rate. While the pre-treatment of samples is very complex, and the analytical instruments used are costly, this

is not something that all laboratories can afford. Therefore, the analysis of emerging contaminants takes a long time from sampling to getting analysis results.

Sensor detection technology is a commonly used on-site detection method in the field of environmental monitoring. It mainly includes electrochemical, optical, and biological sensing. The field rapid detection of emerging contaminants in water environment is a promising research direction. Electrochemical sensing has been extensively studied. Sensor detection technology can give results in minutes for emerging contaminants. However, most of the work was focused on detecting a single contaminant; significant progress has been made in the laboratory, but it has not yet been promoted for field testing; there were fewer examples of field rapid detection of emerging contaminants. Further research is needed on the technology for simultaneously determining multiple emerging contaminants in the meantime.

Immunoassay detection technology is suitable for on-site rapid screening of emerging contaminants in the water environment. Enzyme linked immunosorbent assay can preliminarily screen for the emerging contaminants in the water environment, while immunochromatography can perform qualitative or semi-quantitative detection of emerging contaminants. Immunoassay technology has high specificity, strong sensitivity, simplicity, convenience, and no need for expensive instruments. It has great advantages in rapid detection of large amounts of samples and on-site detection. However, it is prone to false negatives and positives^[89].

There are various types of rapid detection methods for emerging contaminants. Further, the focus of research should be on utilizing new materials to improve traditional detection methods to meet the needs of rapid and on-site detection of contaminants. Besides, researchers could combine multiple detection techniques to make detection methods simpler, faster, and more cost-effective, and with high sensitivity and accuracy to achieve rapid detection of multiple pollutants simultaneously.

KEY WORDS: emerging contaminants; rapid detection; instrument detection; sensor; immunoassay

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