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分子印迹固相萃取技术及其在环境中多环芳烃测定中的应用进展*

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摘要 多环芳烃(Polycyclic aromatic hydrocarbons, PAHs)具有致癌性、致突变性和致畸性等毒性作用,被列为需优先控制的有机污染物.由于持久性和生物蓄积性,环境中存在的PAHs会对人体健康产生不利的影响.本文简要阐述了利用分子印迹聚合物作为吸附剂的固相萃取技术的原理及工作模式,着重介绍了其在环境中多环芳烃检测中的应用进展,并分析了当前存在的问题与应用前景.

关键词 分子印迹, 固相萃取, 多环芳烃, 环境分析, 前处理.

Recent advances of molecularly imprinted solid-phase extraction technique and its application for the determination of polycyclic aromatic hydrocarbons in environment

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Abstract Polycyclic aromatic hydrocarbons (PAHs) are listed as priority organic pollutants due to its potential carcinogenic, mutagenic and teratogenic toxicity. PAHs in the environment have adverse effects on human health because of persistence and bioaccumulation. This study briefly reviews the principal mechanism and the application of molecularly imprinted polymers-based solid-phase extraction technology, especially for the detection of PAHs in environment. The existing problems and application prospects were also discussed.

Keywords molecularly imprinted polymers, solid-phase extraction, polycyclic aromatic hydrocarbons, environment analysis, pretreatment.

多环芳烃(Polycyclic aromatic hydrocarbons, PAHs)是一类具有两个或多个苯环结构的稠环化合物,广泛存在于大气、土壤和水等环境介质中^[1].当前已经发现的PAHs有200多种,多具有致癌性、致突变性、致畸性等毒性作用,其中16种已被美国环境保护署(EPA)列为优先控制的有机污染物^[2].环境中的PAHs主要有两种来源,一是来自火山爆发、森林火灾等自然因素,二是来源于汽车尾气排放和化学燃料不完全燃烧等人为因素^[3].研究表明,人体受到环境中的PAHs的暴露后,可进入消化道、呼吸

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道和皮肤,进而影响人体健康^[4]。同时,PAHs 具有高生物蓄积性,这使得环境中微量 PAHs 暴露也可能会对人体的健康造成严重的威胁^[5]。为了更好地监测环境安全,防止 PAHs 超标带来的环境安全隐患,必须对环境中的多环芳烃进行监测。

目前,已经构建的 PAHs 检测方法包括液相色谱法(LC)^[6]、气相色谱法(GC)^[7]、气相色谱-质谱联用法(GC-MS)等^[8],但由于 PAHs 在大气、水体和土壤中的含量较低,甚至是痕量存在,且环境基质复杂,无论采用何种检测方法,分析复杂环境基质中的痕量 PAHs 均需进行高效且选择性的样品预处理,以便获得更“纯净”的提取物,从而加强样品中多环芳烃的响应度,并减少复杂基质对检测结果的影响。因此,建立快捷、高效的前处理方法对提高测定 PAHs 的效率和增强检测结果的可靠性具有重要意义^[9]。

目前已经广泛应用于环境中 PAHs 前处理的方法有液-液萃取^[10]、索氏提取^[11]和超声辅助提取^[12]等,但这些方法往往存在处理时间长和溶剂消耗多等缺点^[13],更重要的是这些方法缺乏选择性,导致提取后的样品中含有众多的干扰物质,进而会影响测定的灵敏度和重复性。固相萃取技术(Solid-phase extraction, SPE)自 20 世纪 70 年代问世以来,由于操作简便、处理时间短、萃取精度高和易与 LC、GC、GC-MS 等检测仪器联用等优点,已被成功应用于水和土壤中 PAHs 的测定^[14-16]。然而,传统的固相萃取吸附剂材料依然存在特异性低和重现性差的问题,这也限制了其在测定复杂环境基质中 PAHs 的应用。为进一步解决这一问题,亟待寻找特异性高、重复性好的吸附剂材料或方法。近年来,分子印迹聚合物(Molecularly imprinting polymers, MIPs)由于吸附特异性高、制备简单且可重复使用等优点有效弥补了固相萃取传统吸附剂的不足,在 PAHs 检测中显示出良好的应用前景^[17-18]。

本文概述了固相萃取技术、分子印迹聚合物及两者结合应用的原理,着重介绍了其在环境中 PAHs 检测中的应用进展,并分析了当前存在的问题与应用前景,旨在为快速、有效地测定环境中的 PAHs 提供参考。

1 固相萃取技术(Solid-phase extraction technology)

1.1 基本原理

SPE 因成本低、操作简单^[19]在样品前处理领域得到广泛应用,其原理是利用固体吸附剂物理性吸附样品中的目标物质,使其与样品中的“杂质”分离,再利用加热处理或洗脱液洗脱将目标化合物解吸,从而达到有效分离和富集目标化合物的目的^[20]。其中,固体吸附剂对分离和富集目标化合物的效果起着至关重要的作用。常用的固体吸附剂材料包括活性炭、有机高分子树脂、键合硅胶等,但这些吸附剂材料往往存在选择性差的弊端,难以从复杂的样品基质中提取富集“纯净”的化合物,为后续的测定工作带来一定的难度。

1.2 固相萃取技术在环境中 PAHs 检测中的应用

近年来,介孔有机二氧化硅^[21]、介孔二氧化硅纳米颗粒^[22]、碳纳米管^[23]、金属氧化物纳米颗粒^[24]和功能磁性纳米颗粒^[25]等一系列新型 SPE 材料被陆续应用于环境样品中 PAHs 的预处理。Yazdanpanah 等^[26]以 β -环糊精-淀粉复合物为 SPE 材料,结合气相色谱-氢火焰离子化检测器(GC-FID)构建了雨水中 8 种 PAHs(萘、苊、芴、菲、蒽、荧蒽、芘和苯并[a]芘)的检测方法,在 0.1—1000 ng·mL⁻¹范围内具有良好的线性关系,检测限为 0.01—0.07 ng·mL⁻¹,定量限在 0.04—0.24 ng·mL⁻¹,富集因子在 84—95。Nazir 等^[27]使用低成本的废弃茶叶作为 SPE 吸附剂,利用 GC-FID 成功测定了河水中芴、荧蒽、芘、芘和苯并[a]芘的含量,其线性范围为 50—1000 ng·mL⁻¹,回收率为 88.0%—111.4%,相对标准偏差为 1.0%—9.8%。Yang 等^[28]制备了一种新型磁性材料 Fe₃O₄@SiO₂@MMTA-Au 作为 SPE 的吸附剂,从河流和降水中提取富集了 14 种目标 PAHs(萘、芴、苊、菲、芘、蒽、荧蒽、苯并[a]芘、苯并[a]蒽、苯并[b]荧蒽、苯并[k]荧蒽、二苯并[a,h]蒽、茚并[1,2,3-cd]芘和苯并[g,h,i]芘),然后用 HPLC-FLD 测定了各 PAHs 的浓度,其检测限为 0.25—37.5 ng·L⁻¹,回收率为 87.8%—120.0%,富集因子为 80—98。Majd 等^[29]首次合成了一种纳米复合材料作为 SPE 吸附剂,结合 GC-FID 成功应用于土壤、树叶和和水中 PAHs(萘、苊、芴、菲、荧蒽、芘、苯并[a]芘)的提取、富集和含量测定,其线性范围为 5.0—1000 ng·mL⁻¹,检测限为 0.1—0.5 ng·mL⁻¹,回收率为 73.0%—97.1%,相对标准偏差小于 8.0%,富集因子在 46—62。Yan^[30]等合成全氟苯键合硅胶用作 SPE 吸附剂,用于河水和废水中 16 种 PAHs 的

固相萃取,与传统的十八烷基硅胶吸附剂相比,该吸附剂对具有4—6个苯环的PAHs表现出更高的吸附能力,检测限范围为 $0.002\text{--}0.08\ \mu\text{g}\cdot\text{L}^{-1}$,回收率均提高了约20%。上述研究表明,新型吸附剂确实能有效提高SPE的萃取能力,并可应用于实际环境中PAHs的提取,然而该类吸附剂依然存在选择特异性差的弊端,对后续仪器分析定量检测会造成一定影响。

2 分子印迹聚合物 (Molecularly imprinting polymers)

2.1 基本原理

MIPs的制备原理如图1所示,主要涉及模板分子、功能单体、引发剂和交联剂,其中功能单体与模板分子先结合形成配合物,引发剂和交联剂的加入会进一步引发聚合形成高交联度的刚性聚合物,当模板分子被洗脱除去后,聚合物内就会形成与模板分子具有相同形状和大小的空腔^[31]。因此,模板分子与MIPs聚合物内的空腔类似于“分子钥匙”和锁,MIPs空穴内“钥匙分子”的结合位点可以重新识别模板分子并与其结合,从而达到精准选择与分离目标化合物的目的。现有研究表明,MIPs在成分复杂的样品基质中有较高的稳定性,对恶劣的环境具有较好的抵抗性^[32]、选择性和重复利用率。

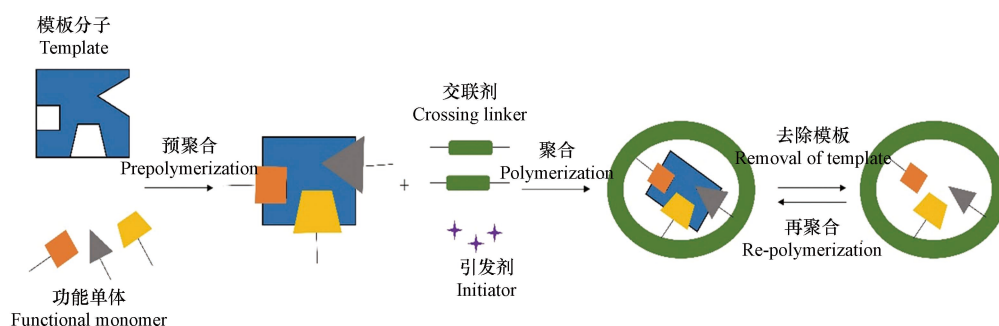


图1 分子印迹聚合物制备的示意图

Fig.1 Illustration on the schematic preparation of the molecularly imprinted polymers

三维网络结构是MIPs的主要结构特征,而功能单体、模板分子、交联剂、引发剂和致孔剂是制备MIPs的必要材料。功能单体在分子印迹中起着至关重要的作用,它们在MIPs的制备和提取过程中需与模板分子和目标分子相结合^[33],因此应选择能与目标分子相结合的功能单体。但当前开发的功能单体还较少,常用的有苯基三甲氧基硅烷、甲基丙烯酸、2-乙烯基吡啶、4-乙烯基吡啶、异丙基丙烯酰胺、乙烯基苯、甲基丙烯酸缩水甘油酯、N-异丙基丙烯酰胺、甲基丙烯酸2-羟乙酯、丙烯酸、丙烯酰胺、甲基丙烯酸甲酯、2-甲基丙烯酸羟乙酯等。模板分子既要能与功能单体相聚合,还需要在洗脱过程中容易去除^[33],因此理想的模板分子不仅要含有与功能单体相互作用的官能团,而且不能干扰聚合反应。此外,不同反应条件(pH、温度等)也可能会影响模板分子的化学稳定性,进而影响MIPs的结构。交联剂是稳定模板分子与功能单体结合位点并赋予聚合物三维结构机械稳定性的重要因素^[33],能保留移除模板分子的记忆;不同的交联剂会导致结合位点的不同,对MIPs的平均粒径和表面均一性也有一定的影响。因此,所选交联剂应该与功能单体具有相似的反应性,且交联剂的浓度不应过低,否则会降低MIPs的机械稳定性,但过高的浓度会减少单位质量MIPs的结合位点数量,且会在交联剂与模板或交联剂与单体之间发生侧向非共价相互作用进而破坏选择性。常用的交联剂有乙二醇二甲基丙烯酸酯、N,N'-亚甲基二丙烯酰胺、二乙烯基苯、四乙氧基硅烷、三羟甲基丙烷三甲基丙烯酸酯、季戊四醇三丙烯酸酯等。引发剂的主要原理是使用自由基来引发聚合反应,这些引发剂通过热分解或紫外线辐射产生自由基,一旦形成,自由基就会通过与所有物质开始连接聚合^[33]。最常用引发剂有偶氮二异丁腈、硅酸乙酯、偶氮二异庚腈、过硫酸钾、过氧化苯甲酰、过硫酸铵、3-溴丙基三甲氧基硅烷等。溶剂主要作用是溶解反应中的所有起始材料,并充当成孔剂,有利于模板分子接近MIPs的结合位点^[33]。溶剂不仅关乎着键的结合强度,还会影响MIPs的形态。一般来说,极性较小的溶剂,如甲苯和二氯甲烷,更加利于增强MIPs的识别能力。

2.2 MIPs 在环境中 PAHs 检测中的应用

目前,已经设计出多种PAHs对应的MIPs^[34-36],并通过不断优化MIPs的特异性以便能更有效地

应用于环境中 PAHs 的检测. Krupadam 等^[18]以甲基丙烯酸为功能单体, 乙二醇二甲基丙烯酸酯为交联剂, 使用 6 种 PAHs 混合物 (苯并 [a] 蒽、苯并 [a] 芘、苯并 [b] 荧蒽、蒽、二苯并 [a,h] 芘、茚并 [1,2,3-cd] 芘) 作为模板, 采用本体聚合法构建了 MIPs, 该材料能有效吸附地下水中的 PAHs, 最大吸附量达 $687 \text{ mg} \cdot \text{g}^{-1}$, 且经 10 次再生实验后, 吸附性能并未受到显著影响. 在后续的研究中^[37], 采用相同的功能单体和交联剂制备 MIPs 微球, 成功从环境水样中选择性分离苯并 [a] 芘, 吸附能力达到 $75 \text{ mg} \cdot \text{g}^{-1}$, 比商业使用的活性炭高出近 300%. 2014 年, Krupadam 等^[38]开发了新的功能性交联剂 N,O-双甲基丙烯酰乙醇胺, 以芘为模板分子构建了 MIPs, 发现该 MIPs 对海水中芘的吸附能力达到 $35 \text{ mg} \cdot \text{g}^{-1}$, 是非模板分子印迹聚合物 (NIPs) 的 9.6 倍, 且对蒽和苯并 [a] 芘的交叉选择性只有 5.5% 和 7.0%. Munawar 等^[39]使用 4-乙烯基吡啶与目标芘进行电聚合形成芘 MIPs 薄膜, 并基于该薄膜设计了一款传感器用于水中 PAHs 的测定, 其检测限达 $0.001 \text{ ng} \cdot \text{L}^{-1}$, 回收率为 83%—110%, 与其他传感器相比, 该基于 MIPs 的纳米膜传感器具有最高的灵敏度. Ncube 等^[40]以苯乙烯为功能单体, 乙二醇二甲基丙烯酸酯为交联剂, 4,4-偶氮(4-氰基戊酸)为引发剂, 使用苯并 [k] 荧蒽和茚并 [1,2,3-cd] 芘为模板分子构建了两种 MIPs, 并将其按照 1 : 1 的比例混合, 用于环己烷溶液中 PAHs 的分离, 结果发现该方法对所有 16 种有毒性的 PAHs 均显示出高选择性和亲和力, 其平均提取效率为 $65\% \pm 13.3\%$, 当溶液中 PAHs 过量时, MIPs 空腔的总体占据程度能达到 $128\% \pm 6.45\%$, 且每个洗脱循环损失率仅为 2.9%; 在后继研究中, 使用该 MIPs 结合膜辅助索氏提取法及 GC-MS 实现了对污泥中的 16 种 PAHs 的测定, 其检测限为 $0.14\text{—}12.86 \text{ ng} \cdot \text{g}^{-1}$, 相对标准偏差值为 0.78%—18%^[41]. Hijazi 等^[42]以 1-乙烯基咪唑为功能单体制备了一种多孔 MIPs 薄膜, 并用作微萃取吸附剂. 结合 GC-MS 检测, 提供了一种适用于测定海水中痕量 PAHs 硫杂环化合物含量的方法. Corman 等^[43]以甲基丙烯酸 2-羟乙基酯为功能单体, 乙二醇二甲基丙烯酸酯为交联剂制备苯并芘 MIPs, 在水中预富集苯并芘的效率为 349.6%, 回收率达到 87.39%.

3 分子印迹固相萃取技术 (Molecularly imprinted solid-phase extraction technology)

3.1 基本原理

分子印迹固相萃取 (Molecularly imprinted solid-phase extraction technology, MISPE) 技术的原理如图 2 所示, 是以分子印迹聚合物为固相萃取吸附剂的固相萃取技术, 克服了传统固相萃取吸附剂选择性差的问题, 可以有效提高目标分子的选择性和吸附能力, 大大降低痕量分子的检测难度^[13]. 采用 MISPE 进行样品预处理包括离线和在线两种模式. 离线模式^[13]包括 MISPE 柱子的调节、样品装载、“杂质”洗涤和目标分子洗脱等 4 个环节, 洗脱液用于 LC、GC 或 GC-MS 等后继分析, 其主要优点是操作简单, 溶剂过量对后续分析的影响较小, 可以充分洗脱目标分子, 但分离、预浓缩等过程中存在目标分子损失和被污染的风险, 且操作过程繁琐耗时, 可能增加后续测定时的误差. 在线模式^[13]实现了 MISPE 的自动化, 即自动加载样品、洗涤“杂质”、洗脱目标分子及检测目标分子的含量, 减少了实际样品的预处理时间, 降低了目标物损失和被污染的风险, 从而提高了检测的准确性和重现性. 然而, 当改变洗脱溶剂的 pH 时可能会对色谱分离造成一定的影响.

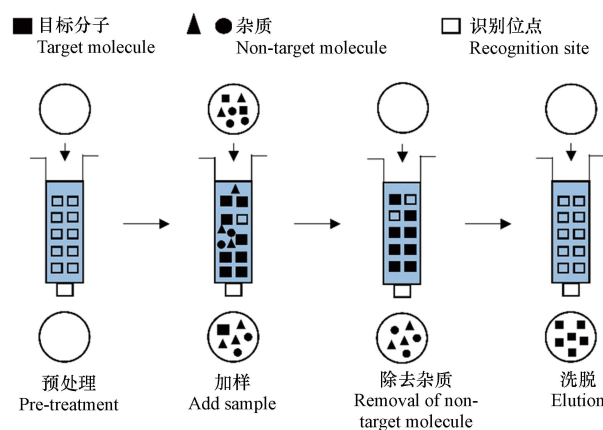


图 2 分子印迹固相萃取技术的原理

Fig.2 Principle of molecularly imprinted polymers-based solid-phase extraction technology.

3.2 新型分子印迹固相萃取方式

3.2.1 基质分散分子印迹固相萃取

2015年,王新鑫等^[44]利用基质分散分子印迹固相萃取技术(MI-MSPD)检测海水中痕量的氯酚,其将磁性MIPs吸附剂与样品通过研磨等方式分散混合后一同填充至固相萃取柱内,再经适当的洗涤步骤除去干扰化合物,最后选用适当溶剂洗脱目标分子.该法所需样品量小,目标分子与洗脱溶剂的接触面较大,溶剂可渗透至样品基质内,有利于充分洗脱目标分子,但研磨的强度、速度和时间等参数对其吸附性能和重复性有较大影响^[45].

3.2.2 磁性分子印迹聚合物固相萃取

1998年,Ansell和Mosbach^[46]首次将分子印迹与磁性铁氧化物相结合制备了具有超顺磁性的磁性分子印迹聚合物微球(MMIPs),并将其应用于溶液中目标分子的吸附.由于MMIPs可在外加磁场作用下实现与溶液的分选,无需过滤或离心等操作,具有操作简单和耗时短的显著优势,在固相萃取领域得到了极大发展^[47].

3.2.3 分子印迹固相微萃取

2001年,Mullet等^[48]首次提出了分子印迹技术固相微萃取技术(MISPME),其将MIPs研磨成具有一定粒度的颗粒并装入毛细管中,利用一套自动的在线装置分析尿液中心得安的含量.SPME主要包含吸附和解吸两个过程,吸附过程中目标分子可在纤维涂层外的固定相中通过物理吸附快速达到平衡分配,后续解吸过程则主要取决于所用的检测方法,如与GC联用时采用通过热解吸方法,而与HPLC联用时则可采用溶剂洗脱.SPME技术操作简便,灵敏度高,吸附材料可重复使用,但对目标分子的选择性较差.搅拌棒吸附萃取(SBSE)是基于与SPME相同的原理,将MIPs吸附剂涂覆在磁力搅拌棒上而实现分离的一种技术,它提供了大量的吸附剂相,有助于提高目标分子的回收率,但平衡时间较长^[49].

3.3 分子印迹固相萃取技术在环境中PAHs检测中的应用

现阶段,基于MIPs的SPE的样品前处理方法已经广泛用于食品和生物领域^[50-53],但在检测环境中PAHs方面仍处于起步阶段.Song等^[54]以苯基三甲氧基硅烷为功能单体,用四乙氧基硅烷作交联剂,乙酸为引发剂,采用16种PAHs标准品为模板分子制备MIPs作为SPE吸附剂,并结合GC-MS成功测定了海水样品中的16种PAHs,其检测限为5.2—12.5 ng·L⁻¹,回收率达83%—113%,相对标准偏差为3.2%—7.5%.李成等^[55]提出了采用16种PAHs标准品为混合模板制备MIPs,并结合SPE与GC-MS实现了对污泥中的多环芳烃的特异性富集、分离与检测,结果显示该方法较为适合测定中环和高环的PAHs.Navarro等^[56]提出基于磁性分子印迹聚合物与高效液相色谱相结合测定河水中16种PAHs的方法,其对亲脂性PAHs的回收率为98.8%—100%,但对亲脂性较低PAHs的回收率较差,为46%—60%;其对葱的检出限最低(1.3 ng·L⁻¹),对萘的检出限最高(969 ng·L⁻¹).Benedetti等^[2]基于沉淀聚合法构建了磁性MIPs固相萃取方法,并与GC-MS相结合用于海水中PAHs的检测,其对低分子量PAHs的回收率为76%—104%,高分子量PAHs的回收率为95%—101%,检出限范围为30—375 ng·L⁻¹,相对标准偏差为3.7%—12.2%.Azizi等^[57]使用甲基丙烯酸和异丙基丙烯酰胺作为双功能单体,以乙二醇二甲基丙烯酸酯为交联剂,偶氮二异丁腈为引发剂,通过沉淀聚合法成功构建了MIPs,结合SPE方法对河水样品进行离线处理后,使用气相色谱-大气压化学电离串联质谱(APGC-MS/MS)测定其中PAHs,结果表明该方法的检出限在1—100 ng·L⁻¹,准确度为72%—135%,且对PAHs的吸附能力高于Fe₃O₄和Fe₃O₄@SiO₂.可以预测,越来越多以PAHs为模板的分子印迹固相萃取技术将应用于环境中的PAHs的检测.

4 结论与展望(Conclusions and prospectives)

MIPs具有选择性高、稳定性好、可重复使用等众多优点,而SPE易与LC和GC等分析仪器联用,因此以MIPs为吸附材料的SPE技术已陆续应用于环境中PAHs的测定.但是,相关研究尚处于起步阶段,有许多问题亟待解决:一是MIPs在制备过程中会用到大量PAHs的模板分子,尽管制备后要经过充分洗脱,但也会有5%左右的模板分子残余在MIPs中,模板分子的泄漏可能会影响痕量化合物后续

检测结果;二是 MIPs 与目标分子的识别和结合主要以氢键作用实现的,而水分子既是氢键受体,又是供体,因此在水溶液中提取目标分子时水分子会竞争性破坏模板和功能单体之间的氢键,导致 MIPs 的识别能力大大降低,从而使得选择性有所下降;三是 MIPs 的吸附容量偏低,且用于制备 MIPs 的功能单体的选择有限.因此,提高模板分子的洗脱率以降低模板分子泄漏对 PAHs 的测定影响,提供更多的吸附位点以增强对 PAHs 分子的识别能力,寻找针对性的功能单体分子以克服 MIPs 在水溶液中的氢键作用,将成为今后针对环境中 PAHs 分子印迹固相萃取技术的重要研究方向.尽管分子印迹固相萃取技术尚存在一定的局限和不足,但鉴于其出色的选择性、稳定性和可重复利用性,其在检测环境中痕量 PAHs 的检测中必将发挥更重要的作用.

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