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评 述 持久性有机污染物研究进展专刊

新型持久性有机污染物分析方法研究进展

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摘要 多溴联苯醚、多溴联苯、全氟辛基羧酸/磺酸、十氯酮和溴代二噁英等属于“斯德哥尔摩公约”2009 年新增列和潜在的持久性有机污染物, 近年来受到环境研究者的广泛关注. 其在环境中的残留特征、污染来源、演变趋势、迁移传输、生物累积和毒理效应方面的研究依赖于分析技术的发展. 多溴联苯醚和多溴联苯与传统持久性有机污染物具有类似的理化性质, 采样和分析测定过程同有机氯农药和多氯联苯相近, 可使用索氏提取、自动索氏提取、超声萃取、微波辅助萃取、压力溶剂萃取等多种提取方法, 酸洗、多层复合层析柱和凝胶渗透色谱是最常用的净化手段, 分析时采用 GC/MS-EI 或 GC/MS-NCI 对指示性单体进行定性定量. 由于环境背景中的残留很低, 使用高分辨质谱和串联质谱可降低方法检出限. 对于水环境和沉积物中的全氟烷基羧酸、磺酸及其盐, 目前主要采用固相萃取 HPLC/MS/MS 测定. 亲水亲油平衡的萃取柱对全氟辛基羧酸和磺酸有良好的回收, 弱阴离子交换萃取柱对短链和长链全氟烷基羧酸和磺酸都有满意的回收. 十氯酮有一定极性, 采用含有丙酮的萃取体系具有较高的回收率, GC/ECD 和 GC/MS 分析时对色谱系统的清洁性有较高的要求, 否则容易导致色谱峰拖尾影响定性和定量. 溴代二噁英与二噁英的分析技术路线类似, 需要更严格的净化过程分离多溴联苯醚, 并在分析时控制热脱溴. 此外, 方法的应用还依靠溴代二噁英标准物质的完善.

关键词
持久性有机污染物
多溴联苯醚
多溴联苯
全氟辛基羧酸/磺酸
十氯酮
溴代二噁英
分析方法

1 引言

2004 年我国加入“斯德哥尔摩公约”后积极履行公约义务, 在首批限定的 12 种持久性有机污染物(POPs)消减与污染防控方面做了大量工作, 得到国际社会的一致认可. 2009 年和 2011 年, “斯德哥尔摩公约”受控名单中分别新增了 9 种和 1 种 POPs, 即: α-六氯环己烷、β-六氯环己烷、五溴联苯醚和八溴联苯醚、十氯酮、六溴联苯、林丹、五氯苯、全氟辛基羧酸、磺酸及其盐和全氟辛基磺酰氟以及硫丹, 并在全球范围开展消减与控制. 潜在的 POPs 还包括, 短链氯化石蜡(SCCPs)、六溴环十二烷(HBCDs)、溴代二噁英、多氯代萘(PCNs)、德克隆(DP)等. 近年来, 新型 POPs 成为环境学研究热点之一. 本文综述了新型 POPs 分析方法学的研究进展.

2 多溴联苯醚

多溴联苯醚(PBDEs)是一类重要的溴代阻燃剂, 由联苯醚溴化生产, 随溴化程度的不同分为五溴联苯醚、八溴联苯醚和十溴联苯醚等产品. 在生产和使用过程中, PBDEs 会进入环境, 并通过长距离迁移造

成大气、水体、沉积物、土壤及生物圈的广泛残留. PBDEs 在环境介质中含量低, 同系物复杂, 需要高效的萃取、良好的净化和高灵敏度的分析仪器才能满足检测要求.

Ali, Chen, Stapleton 等研究了室内外灰尘中的 PBDEs[1~3]、Harrad[4]研究了汽车车内灰尘中的 PBDEs, Cetin[5]研究了窗户玻璃内外壁有机薄层中的 PBDEs. Quiroz[6]研究了大气沉降及雪水中的 PBDEs, Li 等[7]研究了 PBDEs 在城市大气中的垂直分布规律, 杨雪[8]研究了 PM2.5 中的 PBDEs. 树皮、鱼类、鸟类和高营养级生物体中的 PBDEs 也是研究热点[9~12]. Fontanals[13]测定了垃圾渗滤液中的 PBDEs, De Boerd 等[14~16]测定了污水处理厂污水中的 PBDEs. 近年来城市污水处理厂活性污泥中 PBDEs 的研究也得到极大关注[17, 18]. 血清, 母乳是 PBDEs 人体暴露研究的重点, 此外, Kang 等[19, 20]还研究了人体头发中的 PBDEs, Johnson 等[21]研究了人体脂肪中的 PBDEs.

PBDEs 理论上有 209 种同系物, 在联苯醚溴化过程中由于生产工艺、取代能量和空间位阻等效应, 其中 BDE28、47、99、100、153、154、183 和 209 的含量最高, 称为指示性单体, 是目前 PBDEs 最常检测的目标化合物. 此外 BDE25、30、32、33、35、37、66、71、75、77、85、116、118、119、126、138、155、166、181 和 190 也有较高的检出率. 由于十溴联苯醚(BDE209)的产量和用量相比五溴和八溴联苯醚要大得多, 环境中 PBDEs 的残留主要由 BDE209 贡献, 由于 BDE209 不在“斯德哥尔摩公约”受控名录中, 因此 PBDEs 的检测结果常分为 BDE209 和其他单体.

不同区域大气中 PBDEs 的浓度差异很大, 我国的环境背景值在 2.2~15 pg/m^3[22], 广州、香港等城市为 33.8~372 pg/m^3[23], 台州、贵屿等电子垃圾拆解地大气中的浓度可达几个 μg/m^3[24, 25]. 大流量采样器是最常用的采样手段. 利用石英纤维滤膜(QFF)采集颗粒物, 而部分气溶胶和自由态的 POPs 被滤膜后的固体吸附剂(最常用聚氨基甲酸酯泡沫, PUF)吸附, 对于挥发性较强的低溴取代物, 可在二层 PUF 间加装活性碳毡提高采集率.

由于水体中 PBDEs 的浓度通常较低, 液液萃取方法常用于母乳、血清等生物样品的分析[26, 27]. 其缺点是易乳化、操作繁琐、重复性较差. 而微萃取和连续萃取作为液液萃取的补充手段, 具有方便、快捷、萃取效率高的特点, 得到许多研究者的青睐[28]. Fontanals 等[13]利用微孔纤维膜液液微萃取成功测定水中 PBDEs 的含量. 刘芃岩等[29]使用分散液相微萃取(DLLM)技术将采样、萃取和浓缩集成于一体, 用于水体中 PBDEs 的分析. 固相萃取法(SPE)常用于大体积液体样品中 PBDEs 的提取[6, 30], 能有效地从基体中分离待测物, 排除一定的干扰, 并可同时处理多个样品. 此外, 吸附搅拌棒法(SBSE)也用于水样中 PBDEs 的测定, 利用搅拌棒高分子膜吸附 PBDEs, 经热脱附直接进样, 具有富集效率高、重现性好的特点[31].

近年来, 大气和水体中 PBDEs 的被动采样技术得到快速发展[32, 33], Booij 等[34]利用半透膜被动采集海水用于 PBDEs 测定. 被动采样设备简单、成本低廉、便于携带、无需电力, 利于研究大尺度空间范围内 PBDEs 的分布特征. 同时被动采样采集时间比较长, 所得结果是一定时间的累积, 提高了样品的代表性. 但由于对采样体积不能精确定量, 缺乏统一的技术规范, 限制了其大范围推广[35, 36].

对于土壤、沉积物、大气颗粒物、生物样品等固体样品, 高效的萃取方式决定着方法的回收率. 索氏抽提是土壤、沉积物等固体样品中 PBDEs 提取的经典方法, 亦可用于大气采样膜、鱼类和人体组织中 PBDEs 的分析测定[37~39]. 方法的萃取效率高, 没有交叉污染, 缺点是溶剂使用量大, 萃取时间长. 在此基础上衍生出的索氏热提取和连续索氏提取得到越来越多的应用[40, 41]. 一些研究人员利用超声空化作用, 提高 PBDEs 在固液界面间的传输, 实现 PBDEs 的超声提取(SSE)[42, 43], 方法操作简单, 缺点是萃取效率还有待提高. 近年来超声技术与固相萃取或固相微萃取技术联合, 用于鱼类等生物体中 PBDEs 的提取[44]. 微波辅助萃取(MAE)提取固体样品中 PBDEs, 具有快速高效、溶剂用量小、适用范围广的优点[45], 也可用于贻贝、鲑鱼等海洋生物和人体脂肪组织中 PBDEs 的提取[46]. 压力溶剂萃取(PLE)是在较高的温度和压力条件下, 实现固体或半固体样品中 PBDEs 的高效、快速萃取[47, 48], 已被美国 EPA 确认为固体样品中半挥发性有机污染物的标准提取方法[49]. 目前商品化的加速溶剂萃取(ASE)是一种顺序式的压力溶剂萃取方式, 缺点是容易交叉污染.

环境样品组成复杂, 提取后存在大量共萃物, 如腐殖酸、脂类、色素和其他杂质, 需要净化处理. 净

化的效果直接影响着方法的灵敏度和重现性. 沉积物中的单质硫常用还原铜或叔丁基醇/亚硫酸盐去除[50]. 脂类和色素的去除最常用浓硫酸酸洗[9, 38]和凝胶渗透色谱[39, 51], 前者可有效去除含氧化合物, 后者能分离脂肪等大分子干扰. 进一步的净化可利用硅胶、氧化铝、硅藻土、活性炭等层析柱或多层复合层析柱[44, 52, 53]. 在洗脱过程中, 常用非极性的正己烷、石油醚混合丙酮、二氯甲烷、甲苯、乙酸乙酯等溶剂作为洗脱剂[54]. Alaee 等[55]研究表明使用极性较弱的洗脱液如正己烷/二氯甲烷, BDE209 首先流出, 其他 PBDEs 单体随后流出.

气相色谱-质谱结合了毛细管色谱柱高效的分离性能和质谱定性能力强的优点, 成为 POPs 分析最准确可靠的技术之一, 高分辨的磁质谱和低分辨的四级杆质谱在 PBDEs 分析中都得到了广泛应用. 低溴代化合物的分析通常使用非极性或弱极性的柱子, 按不同单体的沸点高低分离, 长度一般为 30 m. 中等极性的色谱柱也能很好的分离不同 PBDEs 单体[54], 最高使用温度相对较低. BDE-209 易在进样口和柱子中热降解, 因此通常采用高压脉冲进样, 选择 10~15 m 非极性、薄液膜的短柱进行分离[40, 54].

PBDEs 定性定量过程中常用电子轰击源(EI), 对碎片$[M-2Br]^+$和M^+进行定性和定量. 但高溴代 PBDEs (八溴代以上)分子量大和稳定性差, 70 ev 的电子束会引起分子碎裂过度, 无法大量生成分子离子, EI 源灵敏度差[54]. 软电离的负化学源(NCI), 对含氯和溴原子的化合物具有高选择性和高灵敏度, 加入甲烷等反应气, 电离能量降低, 可生成较大的碎片离子, 大大提高了灵敏度, 是测定 BDE209 的常用方法[52, 53, 56, 57]. 为提高定量精度, 并校准 PBDEs 在前处理过程中的损失和仪器分析时的热分解问题, 同位素稀释法测定 PBDEs 被广泛应用. 目前剑桥同位素实验室(Cambridge Isotope Laboratories)、威灵顿(Wellington Laboratories) 和 Accustandard 等机构都能够提供 ^{13}C 标记的 PBDEs 标准物质.

除了四极杆低分辨质谱外, 气相色谱-高分辨质谱仪(GC/HRMS)和气相色谱串联四极杆质谱(GC/MS/MS)具有抗干扰能力强、选择性好、灵敏度高的优点, 也被应用于环境中 PBDEs 的分析[58~61]. 此外, 使用气相色谱/电子捕获检测器(GC-ECD)[55]、气相色谱-电感耦合等离子体质谱(GC-ICP/MS)、液相色谱串联质谱、离子阱质谱、串联离子阱质谱、飞行时间质谱测定 PBDEs 的方法也有报道[42, 62~70].

3 多溴联苯

多溴联苯(PolyBrominated Biphenyls, PBBs)也属于溴系阻燃剂, 主要用于热塑型塑料及一些电子电器产品中[71], 其性质和应用与 PBDEs 类似, 但应用范围和用量远不及 PBDEs. 商用产品主要包括六溴、八溴和十溴联苯, 含量最高的单体分别是 BB153、180 和 209, 其中六溴联苯的产量和用量最大[72]. 1973 年美国密歇根州 PBBs 污染事件后, PBBs 逐渐被停止生产使用[73].

目前国内外学者对 PBBs 的研究主要集中于空气、土壤、污水处理厂污泥、湖泊沉积物和鸟蛋、鱼肉、鱼肝、袋獾、母乳、血浆等生物样品[74~83].

BB153 是多溴联苯最重要的指示物, 此外 BB15、18、52、101、180 和 209 也是 PBBs 测定的主要目标物. 由于样品基质复杂, 目标化合物浓度低[84], 样品前处理在整个分析方法中显得尤为重要, 其步骤主要包括样品萃取及净化, 与 PBDEs 分析的技术路线类似. 许多研究者将 PBDEs 和 PBBs 同时测定.

对于土壤、沉积物、污泥、鸟蛋、鱼肉、动物组织等固体样品, 萃取前需脱水并均匀化, 以便贮存和取样, 也利于样品与有机溶剂的充分接触[85]. 脱水可采用无水硫酸钠、硅藻土、硅胶混合样品[86], 或冷冻干燥[87], 也可采用自然风干或热气流风干, 但后者易污染样品. 固体样品常用超声萃取、索氏萃取、微波辅助萃取、超临界流体萃取、压力溶剂萃取等萃取手段, 萃取溶剂常选择甲苯、二氯甲烷、正己烷/丙酮、二氯甲烷/丙酮、二氯甲烷/正己烷等[88~90]. 虽然 PBBs 在正己烷中有良好的溶解性, 但对于污泥、动物组织等基质复杂的样品, 单一正己烷的萃取效率较低, 一般选用极性和非极性的混合萃取剂[91, 92].

对于水样、母乳、牛奶、血清和尿液等液体样品, 液液萃取、固相萃取和固相微萃取等萃取技术应用最多. 美国 EPA 方法 527[93]中采用固相萃取 GC/MS 检测水中 PBBs. 何松洁等[94]建立了液液萃取(异丙醇:正己烷:甲基叔丁基醚 = 2:1:1)-GPC-GC/MS-NCI 测定人血清中 BB-153、1,2-二(2,4,6-三溴苯氧基)乙烷(BTBPE)和德克隆(DP)的方法, 该方法摒弃了传统的浓 H_2SO_4 酸洗过程, 适用范围广, 能同时测定不耐受浓 H_2SO_4 的多种溴系阻燃剂. Polo 等[95]研究了顶空固

相微萃取 GC/MS/MS 测定水中的 PBBs. Thomsen 等采用固相萃取技术检测了人体血清及母乳中的溴系阻燃剂[96, 97]. 刘潇等[98]采用 HLB 固相萃取-多层复合层析柱净化-同位素稀释-GC/MS 检测血清中 8 种 PBBs, 方法检出限为 2~29 pg/mL. Joanna 等[89]采用索式抽提-渗透膜过滤-GPC-多层复合硅胶柱-氧化铝柱净化-同位素稀释-HRGC/MS/MS 分析生物样品中 PBBs. 总之, PBBs 和 PBDEs 样品前处理流程长, 操作复杂, 但对于准确的定量和定性非常必要.

PBBs 仪器检测方法主要有 GC/ECD, GC/MS-EI, GC/MS-NCI, GC/MS/MS, GC/TOF, HRGC/HRMS, GC×GC/MS 等[99]. 虽然 GC/ECD 对多溴代的 PBBs 有非常高的灵敏度, 但由于不可避免的基体干扰, 定性定量能力不足, 只适合 PBBs 理化性质和环境学参数的模拟研究[100]. 四极杆质谱最常用于 PBBs 的测定, 电子轰击源(EI)选择性好, 但灵敏度偏低, 而负化学源(NCI)灵敏度较高. 赵玉丽等[101]建立了脉冲大体积进样-GC/MS-NCI 测定 BB153 的方法, 检出限为 0.2 pg/g, 具有与 GC/HRMS 接近的检出限和分辨能力. HRGC/HRMS 非常适合痕量 PBDEs 及 PBBs 的测定, 但仪器普及率低、成本高, 而 GC/MS/MS 比单级质谱灵敏度高、抗干扰能力强, 是替代高分辨质谱的不错选择. Polo 等[95]采用 GC/MS/MS 测定水中的 PBBs, 方法检出限可达 7.5~9.0 pg/L, 精密度、准确度良好. 汪洋等[90]用 GC×GC/TOF 筛查鱼肉组织中含卤有机污染物, 解决了复杂基质中多种痕量组分分离的难题.

4 全氟化合物

全氟化合物(PFCs)中被列入“斯德哥尔摩公约”的是全氟辛基羧酸(FPOA)、全氟辛基磺酸(PFOS)及其盐和全氟辛基磺酰氟(PFOSF). 由于 C–F 键的键能高、稳定性强, PFCs 很难在环境中降解, 近年来在各环境介质、生物体和人体中均检出了 PFCs, 其中以 PFOA/PFOSs 为主[102], 这主要是由于环境中的氟调醇和磺酰氟等 PFCs 最终转化为 PFOA/PFOSs[103]. 由于环境中 PFOA/PFOSs 的限值很低, 如美国明尼苏达州饮用水中 PFOA 和 PFOS 的最大允许浓度分别为 0.5 和 0.3 μg/L, 新泽西州则将 0.04 μg/L 定为 PFOA 的非致癌限量值[104], 因此 PFOA/PFOSs 的分析方法必须要选择性强、灵敏度高. 目前多选用液相色谱/三重四极杆串联质谱进行测定, 除了 C8 外, C4~C14 全氟羧酸和 C4、C6 全氟磺酸也是常测的目标化合物.

对于沉积物、土壤和灰尘等固体样品, 一般包括干燥、萃取、稀释、富集、净化和浓缩等步骤. Schroder[105]以污泥为基质, 比较了索氏提取、压力溶剂萃取(PLE)和热蒸汽提取的提取效率, PLE 方法最好, 10 种 PFCs 的回收率为 105%~120%. Alzaga 等[106]优化了 PLE 的提取溶剂组成, 使用乙腈/甲醇(1:3, *v*/*v*)提取回收率大于 95%. 然而商品化 PLE(如热电-戴安公司的 ASE)设备中的聚四氟乙烯(PTFE)管路会带来不可避免的背景干扰. 超声萃取不易引入干扰而逐渐成为目前固体样品的主要萃取手段. Higgins 等[107]依次使用 1%乙酸水溶液和 1%乙酸的甲醇水(9:1, *v*/*v*)进行超声萃取后发现, 沉积物和污泥中 12 种 PFCs 的回收率分别为 73%~98%和 41%~91%. 在样品中加入一定量的活性碳, 超声萃取离心后可直接浓缩进样[108]. Stock 等[109]用离子对试剂对沉积物进行提取分析, 13 种 PFCs 的回收率为 62%~138%.

对于水样, 固相萃取法(SPE)是目前应用最为广泛的提取技术, 方法操作简单, 溶剂消耗少, 能同时完成萃取和净化步骤, 可实现自动化操作, 但需避免全自动固相萃取系统中 PTFE 等含氟管路. 另外, 当颗粒物含量较高时, 需预先过滤, 不能实现水相和颗粒相的同时分析. 值得注意的是, 玻璃纤维、尼龙、醋酸纤维和聚醚砜等材质的滤膜上都可能残有 PFCs 而污染样品, 因此 Schultz 等[110]选择离心的方法分离水相和颗粒相. 目前商用的固相萃取柱有多种类型, 潘媛媛等[111]比较了原戴安(DIONEX)公司的二乙烯基苯(PR)柱、聚乙烯吡咯烷酮(P)柱、C18 柱和 WATERS 的亲水亲油平衡(HLB)萃取柱对 9 种 PFCs 的萃取回收率, HLB 柱效果最好, 回收率为 57.3%~118%. Yamashita 等[112]利用 HLB 分析了海水中 7 种 PFCs 的含量, 灵敏度可达 pg/L. 然而 HLB 柱对短链 PFCs 富集效率较低, Taniyasu 等[113]发现弱阴离子交换(WAX)柱对 22 种 PFCs 的总体萃取效果要好于 HLB 萃取柱. Alzaga 等[114]建立了顶空固相微萃取法, 避免了固相萃取污染样品的可能性, 但需要衍生化提高目标物挥发性, 操作较为繁琐. 此外, Zhang 等[115]合成了磁性纳米材料(Fe_3O_4-C18-壳聚糖)用来萃取水样中的 PFCs, 为 PFCs 的分析方法提供了新思路. 近年来, 被动采样技术也广泛应用于水样中 PFOA/PFOSs 的采集, 在两层聚醚砜(PES)膜之间填装二乙烯基苯和 *N*-乙烯吡咯烷酮同聚物吸附材料, 制成极性有机污染物采样

器(POCIS), 适用于 Log *K*ow < 3.5 的化合物. Kaserzon 等[116]对 5 种全氟烷基羧酸和 3 种烷基磺酸进行了研究, 发现浓度为 0.1~12 ng/L 时, 具有良好的重现性.

大气是 PFCs 长距离传输的重要媒介, 而且室内空气中的 PFCs 是人体暴露的重要来源之一[120, 122]. 有研究推断挥发性较强的 PFOA/PFOSs 前体化合物, 如全氟辛基磺酸酯、全氟辛基磺酰醇和全氟辛基磺酰胺等通过长距离传输到达极地, 再降解成为 PFOA/PFOSs [117~119]. Barber 等[120]使用主动采样法分析检测了室内和室外空气中的 PFCs, 用 QFF 采集颗粒相中的 PFCs, PUF-XAD 采集挥发性的 PFCs, 极性的 PFCs 使用 HPLC/Q-TOF 分析, 非极性的用 GC/MS-PCI 分析. Harada 等[121]使用安德森分级采样器研究了不同粒径大气颗粒物上 PFOA/PFOSs 的分布趋势, 显示粒径为 1.1~1.4 μm 的颗粒物吸附了 58.3%~89.8%的 PFOA 和 PFOS. Jahnke 等[122]利用 PUF "三明治"和石英纤维膜采集大气中 FTOHs、FOSAs/FOSEs 等 12 种 PFOA/PFOSs 前体物, GC/MS 分析, 检出限为 0.2~2.5 pg/m^3, 回收率为 61%~115%, 但短链的 FTOH 易穿透固相吸附柱, 通过同位素稀释法可校准方法回收率, 提高精密度.

由于 PFCs 不同于传统的 POPs, 具有较强的极性, 大气被动采样时需要使用涂渍吸收液的吸附盘. Shoeib 等[123]使用被动采样法检测了环境中的 EtFOSA、MeFOSE 和 EtFOSE3 种挥发性的 PFCs, 2011 年[124]验证了该采样方法同样也适用于半挥发性的 PFCs. Goosey 和 Harrad[125]用被动采样法测定了英国室内和室外空气中 8 种 PFCs 的季节变化趋势, 回收率为 68%~77%.

血液和母乳等生物样品分析的关键是去除脂肪、蛋白质等干扰, 常用四丁基铵(TBA)消化, 甲基叔丁基醚(MTBE)萃取, 再净化和浓缩. Ylinen 等[126]采用离子对试剂法对血浆和尿液进行了提取, 碱性条件下加入 TBA, 乙酸乙酯超声萃取, PFOA 的回收率为 96%~110%. Hansen 等[127]改用 MTBE, 摇床振荡提取 3 次, 血清和肝脏样品中的 4 种 PFCs 的提取效率在 56%~101%. 除了液液萃取法, 可采用乙腈沉降蛋白, 离心后测定[128]. Hansen 等[129]考察了甲酸、乙腈和三氯乙酸 3 种有机溶剂沉降血液中蛋白的效果, 表明甲酸效果最好, 提取液经 C18 小柱净化后, 11 种 PFCs 回收率为 64%~112%. 王杰明等[130]对比了离子对试剂、甲酸、甲醇和乙腈 4 种溶剂对牛奶的萃取效率, 以及 WAX 和 HLB 小柱的富集和净化效果, 显示甲醇萃取, WAX 柱富集净化效果最好, l4 种 PFCs 的回收率达 85.4%~120%, 方法检出限 5~92 pg/L. 自动固相萃取在血液和母乳样品的分析中也得到了应用[131, 132], 优点在于操作简单、效率高, 缺点是短链 PFCs 回收率较低, 而且自动化装置中使用耐酸耐碱的 PTFE 部件会引入污染, 用时需要更换. 对于非液状生物样品, 先匀浆, 然后采用液液萃取法[133]或者碱消解法[134]. 样品中脂肪含量较高时, 可适量添加活性碳去除基体干扰[135].

虽然经过衍生化, 全氟烷基羧酸和磺酸及其盐可以用 GC/MS 来测定, 但最常用的检测仪器是 HPLC/MS/MS-ESI. GC/MS 主要用于易挥发的氟代调聚物的测定. 三重四极杆串联质谱技术有效地提高了信噪比, 重复性好, 分析时间短, 对氟代调聚物的分析也有良好的效果[136]. Berger 等[137]对比了离子阱、飞行时间和三重四极杆质谱分析痕量 PFCs 的效果. 相对于串联四极杆质谱, 离子阱质谱的灵敏度较低, 但适用于 PFCs 同分异构体的定性和结构解析, 飞行时间质谱虽然有高选择性和高灵敏度, 但线性范围窄.

痕量 PFCs 分析的另一大难点是全程序空白的控制. ISO 25101[138]和 EPA Method 573[139]中均要求分析过程的空白需小于实际样品浓度的十分之一. 因此, 在 PFCs 样品采集、储存和分析过程中应避免接触 PTFE、全氟橡胶等含氟聚合物, 而这类物质因其具有耐酸耐碱耐热的特性, 在实验用器材和设备中广泛应用. 分析过程中使用的容器必须依次用水和甲醇清洗. HPLC 等仪器和设备中的含氟管路和配件需更换成不锈钢或 PEEK(聚醚醚酮)材质. 进样瓶瓶盖内衬不使用 PTFE, 或采用铝箔阻隔. 由于长链 PFCs 会不可逆的吸附到玻璃表面, 使用聚乙烯(PE)或聚丙烯(PP)材质为佳[140]. 研究表明一些氟代调聚物可以降解成全氟磺酸[141]或全氟羧酸[142], 因此污泥和生物样品采集后应冻干储存, 尽快分析. 痕量 PFCs 的基体效应同样也是一个很难解决的问题, 采用多种形式的净化, 并使用标准替代物和净化内标来校正, 可提高方法的精密度和准确性[122]. Yeung 等[143]分析了血液中的 10 种 PFCs、可提取有机氟化合物(EOF)和总氟的含量, 发现 PFCs 只占 EOF 的一部分, 而 EOF 还不到总氟化合物的 50%, 这表明血液中还有很多未知的含氟化合物需要我们探索和研究.

5 十氯酮

十氯酮(Chlordecone)又名开蓬(Kepone), 是一种人工合成的有机氯杀虫剂, 具有典型 POPs 特征, 历史上广泛用于控制香蕉根蛀虫, 还用于控制马铃薯甲虫、锈螨和烟草切根虫.

与其他有机氯农药不同, 由于羰基的存在, 十氯酮在水溶液中容易形成水合物, 生成偕二醇. 十氯酮在一些常用的有机溶剂中并不能稳定存在[144], 采用核磁共振、红外光谱和质谱也证实了其在甲醇中以半缩醛的形式存在. Gilbert 等[145]研究表明十氯酮与丙酮在回流 18 h 后会发生反应, 十氯酮与丙酮在室温下五周后会发生反应, 但冷藏保存八个月后仅有不到 1%的十氯酮发生反应[146]. 十氯酮在 ECD 上有良好的灵敏度, 溶液中加入 1%左右的甲醇可以提高响应[147~149]. 十氯酮的分析多采用 GC/ECD 和 GC/MS 的方法, 亦有使用 GC/MS/MS[150, 151]、HPLC/MS/MS[152]和近红外反射光谱法[150](NIRS)进行分析的报道. 国内仅有孙翠香等[153]采用索氏提取 GC/MS 的方法测定土壤中十氯酮.

样品中十氯酮的残留通常采用液液萃取[147, 148, 151]、索氏提取[147, 148, 150, 153, 154]和压力溶剂萃取[155]等方法. 由于十氯酮具有一定极性, 正己烷、石油醚等非极性溶剂萃取效率低, 因此常采用含有一定比例的极性溶剂进行提取, 以提高十氯酮的回收率[156].

柱色谱净化时常用的填料是弗罗里硅土、硅胶、氧化铝等吸附剂. 由于十氯酮不耐受浓硫酸, 对于鱼类等复杂基质, 采用浓硫酸去除含氧化合物的方法不可取, 可使用凝胶渗透色谱(GPC)去除大分子干扰. 十氯酮在弗罗里硅土净化柱中有很强的保留性, 在与其他有机氯农药同时分析时不易洗脱, Saleh 等[147]采用 10%甲醇/5%苯的正己烷溶液进行洗脱, Moseman 等[148]采用 1%甲醇/2%乙腈/4%苯的正己烷溶液进行洗脱, 可以达到满意的洗脱效果.

GC/ECD 法对十氯酮的响应很高, 但只依靠色谱的保留时间进行定性会导致假阳性, 气相色谱-质谱法在保持高灵敏度的前提下, 有效克服了基质干扰, 所以在实际检测中常将两种方法结合在一起使用. HPLC/MS/MS 分析十氯酮的灵敏度要高于 GC/MS/MS[156]. Brunet 等[150]建立了 NIRS 方法测定土壤中的十氯酮, 与 GC/MS 相比, NIRS 不需要复杂的样品前处理过程, 具有快速、价廉等特点, 通过对比发现两种方法具有很好的相关性.

6 溴代二噁英

溴代二噁英(PBDD/Fs)是结构和毒性与二噁英(PCDD/Fs)相似的一类化合物, 理论上讲, 也有 210 种同类物. 由于溴原子半径比氯原子大, C–Br 键键能比 C–Cl 键弱, 故 PBDD/Fs 比 PCDD/Fs 具有更高的分子量、更高的熔点、更低的水溶性, 以及更低的饱和蒸气压, 意味着 PBDD/Fs 比 PCDD/Fs 更易在生物体内富集[157, 158], 甚至比 PCDD/Fs 毒性更强[159]. 研究其在环境中的污染特征、时空分布、迁移转化等环境行为时, 最大的技术难点在于 PBDD/Fs 的精确定量.

PBDD/Fs 的分析技术研究起步于 20 世纪 80 年代[160, 161], 而国内的研究则刚刚起步. 原因一是 PBDD/Fs 在环境中含量极低, 样品基质干扰大, 准确定量需要复杂的前处理程序和高灵敏度高分辨率的仪器; 二是商品化的 PBDD/Fs 标准物质十分有限, 使得可测定的目标物种类和同位素稀释技术的应用受到局限. 近年来, 加拿大的 Wellington 实验室和美国的剑桥同位素实验室(CIL)在逐步扩充 PBDD/Fs 标准品的种类, 但相比 PCDD/Fs 还是少得多. Hagenmaier 等[162]报道了污泥中 1~5 溴代 PBDD/Fs 的浓度, Wiberg 等[163]报道了大马哈鱼和人乳中 2~5 溴代 PBDD/Fs 的浓度, 但更多报道关注 4~8 溴代 PBDD/Fs. 同 PCDD/Fs 一样, 2,3,7,8 位溴代的组分具有高生物毒性. 目前环境样品中 PBDD/Fs 分析的前处理手段与 PCDD/Fs 类似. 索氏提取和压力溶剂提取技术在 PBDD/Fs 提取方面发挥着主要作用, 浓硫酸酸洗或硫酸硅胶柱、多层复合硅胶柱、氧化铝柱、Florisil 柱、活性炭硅胶柱等层析净化手段普遍采用[164, 165]. Ebert 等[166]优化了上述材料在 PBDD/Fs 分析中的条件. 硫酸酸洗可以去除样品基质中的脂质、还原性物质和多环芳烃等; 硅胶柱可以吸附样品基质中的极性杂质, 而不保留弱极性的 PBDD/Fs; 氧化铝柱可以去除 PCBs 等 POPs 的干扰; Florisil 和活性炭硅胶柱[167]都可以去除多溴联苯醚(PBDEs). 仪器分析方面, 基于同位素稀释 HRGC/HRMS 的分析体系是目前世界公认的“金标准”, 同位素稀释技术确保经过复杂的前处理过程后, 能够准确对目标化合物进行定量. 双聚焦磁质谱以其高灵敏度和高分辨率, 在超痕量、多组分 PBDD/Fs 的分析中具有不可替代的地位. 当然, 也有研究者使用 GC/MS/MS 建立 PBDD/Fs 的分析方法[168], 作为一种备选手段.

尽管 PBDD/Fs的分析方法在不断完善, 但仍然存在一些困难: (1) 高溴代 PBDD/Fs 在色谱进样口和色谱柱分离过程中容易高温分解, 造成灵敏度明显低于低溴代 PBDD/Fs, 这也是目前大部分文献中没有报道高溴代 PBDD/Fs 数据的原因[161~170]; (2) 样品中残存的 PBDEs在仪器分析时会转化成 PBDD/Fs, 造成结果偏高; (3) 已开发出的 PBDD/Fs 标准物质少, 对目标化合物逐一定性定量非常困难. 对于上述技术难点, 可采取的措施: (1) 使用耐高温的薄液膜短色谱柱, 减少化合物在固定液中的分配和在色谱柱中的停留时间, 同时辅以脉冲高压进样来降低化合物在进样口的驻留, 减少高溴代化合物的热分解. 低溴代 PBDD/Fs 使用长色谱柱(60 m)分析, 高溴代 PBDD/Fs 用短柱(15 m), 同时采用冷柱头进样方式防止 PBDD/Fs 分解, 也可采用 HPLC/MS/MS 来分析高溴代组分; (2) 使用 Florisil 或活性炭硅胶柱分离去除干扰测定的 PBDEs 类杂质, 或使用精确质量数来区分 PBDEs 和 PBDD/Fs 的碎片离子. Hagberg[171]综合使用上述技术, 建立了一套分析 4~8 溴代 PBDD/Fs 的方法体系, 优化了样品提取、净化、仪器条件等各项参数, 使溴代二噁英的分析取得了长足进展.

7 结论

以上阐述的方法都是基于传统意义上的方法学, 经提取、浓缩和净化等复杂的样品前处理后, 使用 GC/MS 或 HPLC/MS 等仪器进行定性和定量, 方法的重现性好、灵敏度高、假阳性率低, 是痕量新型 POPs 精确测定和仲裁分析的首选. 然而近年来生物检测法发展迅速, 酶联免疫法、报告基因法都成功用于 POPs 的分析, 具有成本低、快速、半定量的特性, 是经典测定方法的有力补充.

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Review on the analytical methods of emerging persistent organic pollutants

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Abstract: Polybrominated diphenyl ethers (PBDEs), polybrominated biphenyls (PBBs), perfluorooctanoic acid (PFOA), perfluorooctyl sulfonates (PFOS), chlordecone and polybrominated dibenzo-*p*-dioxin and dibenzofurans (PBDD/Fs), as the new listed POPs in Stockholm Convention and emerging POPs, were increasingly concerned by environmental scientists. The research work about the residue's characteristic, source analysis, trends evolution, transport, bioaccumulation, and toxic effects of these emerging chemicals depended on the development of the analytical methods. Analytical procedures of PBDEs and PBBs were similar to those of organochlorine pesticides (OCPs) and poly chlorinated biphenyls (PCBs), due to their similar physical and chemicalcharacteristics with "Dirty Dozen". Many extraction methods, such as Soxhlet extraction, automatic Soxhlet extraction, supersonic extraction, microwave assisted extraction, pressurized fluid extraction, were applied for water, sediment, soil and particulate matter. Common clean-up steps were sulfuric acid silica gel cartridge, multiple layer chromatography column and GPC. Although HRGC/HRMS and GC/MS/MS were effective for environmental background samples, GC/MS-EI and GC/MS-NCI were most popular for determinations of the PBDEs and PBBs indicators or markers. HPLC/MS/MS with solid phase extraction was developed for the perfluorinated alkyl acids, sulfonates and their salts. HLB solid phase column was efficient for PFOA/PFOSs recoveries from water samples, as the weak anion exchange column could raise the recoveries of perfluorinated alkyl acids and sulfonates with the carbon chain ranging from 4 to 14. Acetone was necessary in the extraction because of the polarity of clordecone. The GC injector and capillary column needed cleaning carefully when clordecone was analyzed by GC/ECD and GC/MS, otherwise the strong tailing of chromatographic peak would make the exact qualitative and quantitative impossible. The analysis procedures for polybrominateddibenzo-p-dioxin and dibenzofurans (PBDD/Fs) were similar to those of PCDD/Fs. Florisil or active carbon-impregnated silica gel column were packed to separate PBDEs and PBDD/Fs. The instrumental conditions were optimized to prevent from the thermal degradation of higher brominated compounds. The application of the method was also depended on the improvement of PBDD/Fs reference materials.

Keywords: persistent organic pollutants (POPs), polybrominated diphenyl ethers (PBDEs), polybrominated biphenyls (PBBs), perfluorooctanoic acid/sulfonates (PFOA/PFOS), chlordecone, polybrominated dibenzo-*p*-dioxin and dibenzofurans (PBDD/Fs), analytical method